

PATENT ABSTRACTS OF JAPAN

DISCLOSES

(11)Publication number : 07-321339
 (43)Date of publication of application : 08.12.1995

CATALYST
 CONCENTRATION

(51)Int.Cl. H01L 29/786
 H01L 21/20
 H01L 21/205
 H01L 21/268
 H01L 27/12

(21)Application number : 06-164643
 (22)Date of filing : 22.06.1994

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(30)Priority

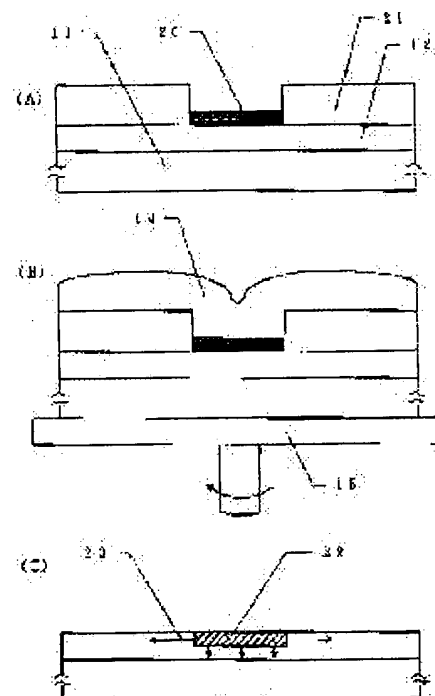
Priority number : 05180752 Priority date : 25.06.1993 Priority country : JP
 06 36616 08.02.1994 JP

(54) SEMICONDUCTOR DEVICE AND MANUFACTURE THEREOF

(57)Abstract:

PURPOSE: To obtain a crystalline silicon thin film with improved grain size and orientation controllability at relatively low temperature with high productivity, by forming the crystal growth surface of the non-single-crystal silicon semiconductor film having crystallinity, to be formed on a substrate, almost into a (111) plane.

CONSTITUTION: A silicon oxide film 21 to be a mask is formed on an amorphous silicon film 12 on a glass substrate 11. The silicon oxide film 21 is patterned to obtain a required pattern, and a thin silicon oxide film 20 is formed by ultraviolet irradiation in an oxygen atmosphere. Then the entire surface of the substrate is spin-coated with an acetate solution containing nickel to form a uniform liquid film 14. Heat treatment is performed to accelerate crystallization of the amorphous silicon film 12. During this process, a crystal horizontally grows from the region 22 with nickel implanted to the region with no nickel implanted as shown by the arrow 23. Thereafter, the cover silicon oxide is stripped using buffer hydrofluoric acid, and laser crystallization is performed. Thus a highly (111)-oriented film is obtained.



LEGAL STATUS

[Date of request for examination]	26.08.1994
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	2791858
[Date of registration]	19.06.1998
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

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CLAIMS

[Claim(s)]

- [Claim 1] It is the semiconductor device which is a semiconductor device using the non-single crystal silicon semiconductor film which has the crystallinity established on the substrate, and is characterized by a crystal-growth side being an outline (111) side.
- [Claim 2] It is the semiconductor device which the catalyst metal contains in the non-single crystal silicon semiconductor film which is a semiconductor device using the non-single crystal silicon semiconductor film which has the crystallinity established on the substrate, and has the aforementioned crystallinity, and is characterized by a crystal-growth side being an outline (111) side.
- [Claim 3] The semiconductor device characterized by using a kind or two or more kinds of elements which were chosen from nickel, Pd, Pt, Cu, Ag, Au, In, Sn, Pb, As, and Sb as a catalyst element in a claim 2.
- [Claim 4] It is the semiconductor device characterized by a catalyst element being an invaded type element to silicon in a claim 2.
- [Claim 5] The semiconductor device with which concentration of a catalyst element is characterized by being 1×10^{16} atoms cm^{-3} - 1×10^{19} atoms cm^{-3} in a claim 2.
- [Claim 6] the semiconductor device using the non-single crystal silicon semiconductor film which has the crystallinity established on the substrate -- it is -- the aforementioned semiconductor film -- a substrate front face -- an outline -- the semiconductor device characterized by carrying out the crystal growth in the parallel direction, and the aforementioned crystal-growth direction carrying out outline coincidence of the direction to which the carrier in the aforementioned crystal-growth direction and the aforementioned semiconductor device moves in accordance with outline <111> shaft orientation
- [Claim 7] the semiconductor device using the non-single crystal silicon semiconductor film which has the crystallinity established on the substrate -- it is -- the aforementioned semiconductor film -- a substrate front face -- an outline -- the semiconductor device characterized by carrying out outline coincidence of the direction which has the grain boundary along an parallel direction and met the aforementioned grain boundary, and the direction to which the carrier in the aforementioned semiconductor device moves
- [Claim 8] the semiconductor device using the non-single crystal silicon semiconductor film which has the crystallinity established on the substrate -- it is -- the aforementioned semiconductor film -- a substrate front face -- an outline -- the semiconductor device characterized by to carry out the crystal growth in the parallel direction, and for the aforementioned crystal-growth direction to have high conductivity to other directions, and to carry out outline coincidence of the aforementioned crystal-growth direction and the direction to which the carrier in the aforementioned semiconductor device moves
- [Claim 9] the TFT using the non-single crystal silicon semiconductor film which has the crystallinity established on the substrate -- it is -- the aforementioned semiconductor film -- a substrate front face -- an outline -- the semiconductor device characterized by carrying out the crystal growth in the parallel direction, and carrying out outline coincidence of the aforementioned crystal-growth direction and the direction of the carrier which flows in the channel of aforementioned thin film TORANJITA
- [Claim 10] the TFT using the non-single crystal silicon semiconductor film which has the crystallinity established on the substrate -- it is -- the aforementioned semiconductor film -- a substrate front face -- an outline -- the semiconductor device characterized by carrying out the crystal growth in the parallel direction, and for the aforementioned crystal-growth direction having outline <111> shaft orientations, and carrying out outline coincidence of the aforementioned crystal-growth direction and the direction of the carrier which flows in the channel of aforementioned thin film TORANJITA
- [Claim 11] the semiconductor device using the non-single crystal silicon semiconductor film which has the crystallinity established on the substrate -- it is -- the aforementioned semiconductor film -- a substrate front face -- an outline -- an parallel direction -- a crystal growth -- carrying out -- **** -- a semiconductor device -- the aforementioned substrate front face -- an outline -- the semiconductor device characterized by to be formed in the parallel direction at the staging area of the crystal growth of the crystalline silicon film which carried out the crystal growth, and to carry out the outline coincidence of the aforementioned crystal-growth direction and the direction to which the carrier
- [Claim 12] The process which introduces into one field of an amorphous silicon film the catalyst element which promotes crystallization. The process which it heat-treats [process] and crystallizes some or all of the aforementioned amorphous silicon film. The process which irradiates a laser beam or strong light at the silicon film which the above part or all crystallized. It is the semiconductor device production method equipped with the above, and is characterized by controlling the stacking tendency of the aforementioned silicon film by controlling the rate of crystallization by the aforementioned heating, the aforementioned laser beam, or the rate of crystallization by irradiation of strong light.
- [Claim 13] The process which introduces into one field of an amorphous silicon film the catalyst element which promotes crystallization. The process which it heat-treats [process] and crystallizes some or all of the aforementioned amorphous silicon film. The process which irradiates a laser beam or strong light at the silicon film which the above part or all crystallized. It is the

semiconductor device production method equipped with the above, and by controlling the rate of crystallization by the aforementioned heating, the aforementioned laser beam, or the rate of crystallization by irradiation of strong light, the stacking tendency of the aforementioned silicon film is controlled and it is characterized by performing control of the rate of crystallization by the aforementioned heating with the amount of introduction of the aforementioned catalyst element.

[Claim 14] The process which introduces into one field of an amorphous silicon film the catalyst element which promotes crystallization. The process which it heat-treats [process] and crystallizes some or all of the aforementioned amorphous silicon film. The process which irradiates a laser beam or strong light at the silicon film which the above part or all crystallized. It is the semiconductor device production method equipped with the above, and by controlling the rate of crystallization by the aforementioned heating, the aforementioned laser beam, or the rate of crystallization by irradiation of strong light, the stacking tendency of the aforementioned silicon film is controlled and it is characterized by control of the rate of crystallization by the aforementioned heating being performed by the temperature and/or time of the aforementioned heating.

[Claim 15] The process which introduces into one field of an amorphous silicon film the catalyst element which promotes crystallization. The process which it heat-treats [process] and crystallizes some or all of the aforementioned amorphous silicon film. The process which irradiates a laser beam or strong light at the silicon film which the above part or all crystallized. It is the semiconductor device production method equipped with the above, and by controlling the rate of crystallization by the aforementioned heating, the aforementioned laser beam, or the rate of crystallization by irradiation of strong light, the stacking tendency of the aforementioned silicon film is controlled and it is characterized by control of the rate of crystallization by the aforementioned laser beam or strong light being performed by the aforementioned laser beam or the irradiation intensity of strong light, and/or irradiation time.

[Claim 16] The semiconductor device equipment production method characterized by providing the following. The process which introduces the catalyst element which promotes crystallization of an amorphous silicon film on the substrate which has an insulating front face. The process which forms an amorphous silicon film on the substrate into which the aforementioned catalyst element was introduced. The process which it heat-treats [process] and crystallizes some or all of the aforementioned amorphous silicon film. A laser beam or strong light is irradiated, it has the process which obtains a crystalline silicon film, and the aforementioned crystalline silicon film is outline (111) orientation.

[Claim 17] The process which introduces the catalyst element which promotes crystallization into some fields of the process which forms an amorphous silicon film on the substrate which has an insulating front face, and one field of the aforementioned amorphous silicon film, The process which makes it perform a crystal growth in the direction parallel to the aforementioned substrate from the field where it heat-treated and the aforementioned catalyst element was introduced, The semiconductor device production method characterized by controlling the stacking tendency of a silicon film by having the process which irradiates a laser beam or strong light on the silicon film with which the aforementioned crystal growth was made, and controlling the thickness of the aforementioned amorphous silicon film.

[Claim 18] The process which introduces into one field of an amorphous silicon film the catalyst element which promotes crystallization. The process which it heat-treats [process] and crystallizes some or all of the aforementioned amorphous silicon film. The process which irradiates a laser beam or strong light at the silicon film which the above part or all crystallized. It is the semiconductor device production method equipped with the above, and particle size of the aforementioned silicon film is characterized by being controlled by controlling the amount of introduction of the catalyst element which promotes the aforementioned crystallinity, and/or the temperature of heat-treatment.

[Claim 19] The process which introduces into one field of an amorphous silicon film the catalyst element which promotes crystallization. The process which it heat-treats [process] and crystallizes some or all of the aforementioned amorphous silicon film. The process which irradiates a laser beam or strong light at the silicon film which the above part or all crystallized. It is the semiconductor device production method equipped with the above, and particle size of the aforementioned silicon film is characterized by being controlled by controlling the amount of introduction of the catalyst element which promotes the aforementioned crystallinity, and/or the time of heat-treatment.

[Claim 20] The semiconductor device production method characterized by using a kind or two or more kinds of elements which were chosen from nickel, Pd, Pt, Cu, Ag, Au, In, Sn, Pb, As, and Sb as a catalyst element in a claim 12 or a claim 19.

[Claim 21] The semiconductor device production method characterized by using an invaded type element to silicon as a catalyst element in a claim 12 or a claim 19.

[Claim 22] The semiconductor device production method that concentration of a catalyst element is characterized by being 1×10^{16} atoms cm^{-3} - 1×10^{19} atoms cm^{-3} in a claim 12 or a claim 19.

[Claim 23] It is the crystalline silicon film formed on the substrate which has an insulating front face. It is the semiconductor which is carrying out the crystal growth of the aforementioned crystalline silicon film from the catalyst element which promotes crystallization introduced into the interface with the aforementioned substrate, and is characterized by carrying out outline (111) orientation of the aforementioned crystalline silicon film.

[Claim 24] It is the semiconductor device characterized by being the semiconductor device which has a crystalline silicon film, and adding the catalyst element with which orientation (111) ratios are 0, and 33-1, and, as for the aforementioned silicon film, promote crystallization in the aforementioned silicon film.

[Claim 25] The portion which it is the semiconductor device which has the crystalline silicon film formed on the substrate which has an insulating front face, and the aforementioned crystalline silicon film has the portion which carried out the crystal growth in the direction parallel to a substrate, and carried out [aforementioned] the crystal growth is a semiconductor device characterized by adding the catalyst element which orientation (111) ratios are 0.67-1, and promotes crystallization in the aforementioned

crystalline silicon film.

[Claim 26] It is the semiconductor device which has the crystalline silicon film formed on the substrate which has an insulating front face, and the aforementioned crystalline silicon film has the portion which carried out the crystal growth in the direction parallel to a substrate, and is characterized by for the orientation (111) ratios of the portion which carried out the crystal growth to be 0.72-1, and to be added the catalyst element which the thickness of the aforementioned crystalline silicon film is 800Å or less, and promotes crystallization in the aforementioned crystalline silicon film

[Claim 27] It is the semiconductor device characterized by being a semiconductor device with the crystalline silicon film with which the catalyst element which promotes crystallization was introduced, and controlling the particle size of the aforementioned crystalline silicon film by the amount of introduction of the catalyst element which promotes the aforementioned crystallinity.

[Claim 28] The semiconductor device characterized by using a kind or two or more kinds of elements which were chosen from nickel, Pd, Pt, Cu, Ag, Au, In, Sn, Pb, As, and Sb as a catalyst element in a claim 23 or a claim 27.

[Claim 29] The semiconductor device characterized by using an invaded type element to silicon as a catalyst element in a claim 23 or a claim 27.

[Claim 30] The semiconductor device with which concentration of a catalyst element is characterized by being 1×10^{16} atoms cm^{-3} - 1×10^{19} atoms cm^{-3} in a claim 23 or a claim 27.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the composition and its production method of the semiconductor device which used the thin film semiconductor. For example, it is related with the composition, the body equipment, and its production method of TFT (TFT) prepared on insulating substrates, such as glass.

[0002]

[Description of the Prior Art] The TFT (following TFT etc.) using the thin film semiconductor is known. This TFT forms a thin film semiconductor on a substrate, and is constituted using this thin film semiconductor. Although this TFT is used for various integrated circuits, it attracts attention as the switching element especially formed in each pixel of electro-optics equipment, especially an active matrix type liquid crystal display, and a driver element formed in the circumference circuit portion which drives a pixel further.

[0003] It is common to use a thin film-like silicon semiconductor to TFT used for these equipments. It is divided roughly into two although it consists of a silicon semiconductor which has what consists of an amorphous silicon semiconductor (a-Si), and crystallinity as a thin film-like silicon semiconductor. Since it was rich in mass-production nature, although the amorphous silicon semiconductor had low production temperature, and it was possible to have produced comparatively easily by the gaseous-phase method, and it was most generally used, since physical properties, such as conductivity, are inferior compared with the silicon semiconductor which has crystallinity, in order to acquire a high-speed property from future, establishment of the production method of TFT which consists of a silicon semiconductor which has crystallinity was called for strongly. In addition, the semi amorphous silicon which has the middle state of polycrystal silicon, microcrystal silicon, the amorphous silicon containing a crystal component, crystallinity, and amorphous nature as a silicon semiconductor which has crystallinity is known.

[0004] As the method (1) of obtaining the silicon semiconductor of the shape of a thin film which has these crystallinity The film which has crystallinity at the time of membrane formation is formed directly.

(2) Form the amorphous semiconductor film and make crystallinity have by the energy of a laser beam.

(3) Form the amorphous semiconductor film and make crystallinity have by applying heat energy.

The said method is learned.

[0005] however, the method of (1) is difficult to go on the whole surface across the film which has good semiconductor physical properties on a substrate, and to form membranes uniformly technically, and there is a problem of the cost which will be said if it cannot use a cheap glass substrate with 600 degrees C or more, since membrane formation temperature is high. Moreover, when the excimer laser currently present most generally used is taken for an example, since the irradiation area of a laser beam is small, the method of (2) has first the problem that a throughput is low, and is not enough to process the whole surface of a large area substrate uniformly, and admiration called the technology of the next generation is strong [the method]. [of the stability of laser] Although there is an advantage that the method of (3) can respond to a large area as compared with the method of (1) and (2), if it is required to make it too the elevated temperature of 600 degrees C or more as heating temperature and it considers using a cheap glass substrate, it is necessary to lower heating temperature further. Especially, in the case of the present liquid crystal display, big screen-ization is progressing, and, for the reason, a glass substrate needs to use a large-sized object similarly. Thus, in using a large-sized glass substrate, a thing called the shrinkage and distortion in a heating process indispensable to semiconductor production lowers precision, such as mask alignment, and serves as a big trouble. In the case of Corning 7059 glass currently present most generally used especially, a point [distortion] is 593 degrees C and big deformation will be caused by the conventional heating crystallization method. Moreover, since the heating time which crystallization takes in the present process besides the problem of temperature reaches in dozens of hours or more, it is also required to shorten the time further.

[0006] And since the silicon thin film which has the crystallinity produced by these methods as a still bigger problem was based on the crystal growth from accidental karyogenesis and there, it was that the particle size, a stacking tendency, etc. can hardly control. Very many attempts which are going to control these are performed over present from the past, and can mention a patent as shown in Japanese Patent Publication No. 5-71993 as the example. However, also in a method as shown in this patent, it is actual that do not pass over **** using the accidental nucleus within a certain limited limits, and did not necessarily control a membranous stacking tendency completely, and control of particle size is not performed at all.

[0007]

[Problem(s) to be Solved by the Invention] this invention offers a means to solve the above-mentioned problem. In the production method of a thin film which consists of a silicon semiconductor using the method of crystallizing the thin film which more

specifically consists of amorphous silicon by heating which has crystallinity, it sets it as the purpose to offer the process which is compatible in low-temperature-izing of temperature required for crystallization, and shortening of time. Of course, the silicon semiconductor which has the crystallinity produced using the process offered by this invention has what was produced with the conventional technology, and the physical properties more than equivalent, and it is a thing needless to say that it is usable also to the barrier-layer field of TFT.

[0008] The production method of the crystalline new silicon thin film replaced with the method which used the conventional accidental karyogenesis on that occasion is offered. While this method is the production method of the crystalline silicon thin film which has sufficient productivity in low temperature comparatively, it is a method of having control of particle size, and a controllability quite high also about a stacking tendency.

[0009]

[Means for Solving the Problem]

[Background of invention] This invention people performed following experiments and considerations that the control method of the method of promoting heat crystallization, particle size, and a stacking tendency should be considered in order to solve the trouble which accompanies crystallization of amorphous silicon which was stated by the term of the above-mentioned Prior art.

[0010] First of all, how to promote heat crystallization is described. First, as an experiment fact, when the mechanism which an amorphous silicon film is formed [mechanism] on a glass substrate, and crystallizes this film by heating was investigated, the crystal growth began from the interface of a glass substrate and amorphous silicon, and the perpendicular thing gone on pillar-shaped was accepted to the substrate front face more than to a certain amount of thickness.

[0011] The crystalline nucleus (kind used as the basis of a crystal growth) used as the basis of a crystal growth exists in the interface of a glass substrate and an amorphous silicon film, and the above-mentioned phenomenon is considered to originate in a crystal growing from the nucleus. It is thought that such a crystalline nucleus is a thing resulting from the crystal component (it is thought that the crystal component of oxidization silicon exists in the glass-substrate front face so that it may be called the glass ceramics) or stress on an impurity metallic element or the front face of glass which exists in the substrate front face at the minute amount.

[0012] Then, by introducing a crystalline nucleus more positively, that it should think that low-temperature-izing of crystallization temperature will be possible, and the effect should be checked, other metals were formed on the substrate in the minute amount, and the experiment which performs membrane formation and its afterbaking crystallization for the thin film which consists of amorphous silicon on it was tried. Consequently, when some metals were formed on a substrate, the fall of crystallization temperature was checked, and it was suggested that the crystal growth which used the foreign matter as the crystalline nucleus has happened. Then, the mechanism was investigated in more detail about two or more impurity metals for which low-temperature-izing was possible.

[0013] Crystallization can be divided into an early nucleation and two stages of the crystal growth from the nucleus, and can be considered. Here, although the speed of an early nucleation was observed by measuring time until a detailed crystal occurs in punctiform in constant temperature, in any case, it was shortened in the thin film by which this time formed the above-mentioned impurity metal, and the effect over the formation of crystallization temperature low temperature of crystalline-nucleus introduction was checked. And although it was unexpected, in crystallization of the amorphous silicon thin film which formed it on it after forming a certain kind of metal when heating time was changed and the grain growth after nucleation was investigated, it was observed that even the speed of the crystal growth after nucleation increases by leaps and bounds. About this mechanism, it will state in detail a back forge fire.

[0014] make it any -- the temperature of 580 degrees C or less which was not able to consider conventionally the thin film which formed a certain kind of metal upwards in the minute amount, and consists of amorphous silicon according to the two above-mentioned effects when [that] afterbaking crystallization was carried out, membrane formation and -- 4 It became clear that as sufficient in time of a degree crystallinity as time is acquired. In the impurity metal which has such an effect, an effect is the most remarkable, and the material which we chose is nickel.

[0015] If nickel gives an example for what effect it has, will not process at all. The thin film which consists of amorphous silicon formed by the plasma CVD method on the substrate which is not forming the thin film [minute amount / nickel] (Corning 7059) namely, by heating in nitrogen-gas-atmosphere mind Although 10 hours or more were needed as heating time when crystallizing, and it considered as 600 degrees C as the heating temperature, when the thin film which consists of amorphous silicon on the substrate which formed the thin film [minute amount / nickel] was used, ** which acquires the same crystallization state in heating of about 4 hours was made. in addition, judgment of crystallization in this case -- Raman -- a spectrum -- the spectrum was used Probably, it turns out that the effect of nickel is very large only also from this.

[0016] When the upper shell which formed the thin film [minute amount / nickel], and the thin film which consists of amorphous silicon are formed so that the above-mentioned explanation may show, shortening of the time which low-temperature-izing and crystallization of crystallization temperature take is possible. Then, still more detailed explanation will be added a premise [using this process for manufacture of TFT]. in addition, although the back is explained in full detail, since not only a substrate top but having the effect of low-temperature-izing similarly even if it forms membranes on amorphous silicon and an ion implantation were the same, the thin film of nickel will call processing of these series "nickel minute amount addition" on these specifications from now on -- it is made things

[0017] The method of nickel minute amount addition is explained first. Minute amount addition of nickel has the effect of low-temperature-izing by the method of forming amorphous silicon previously and forming a minute amount nickel thin film from it also by the method of forming a minute amount nickel thin film and forming amorphous silicon after that on a substrate, as well

as both, plasma treatment of a vacuum deposition is also possible for the membrane-formation method also at a spatter, and not asking has made the membrane-formation method clear. Plasma treatment is the method of adding a catalyst element on an amorphous silicon film by producing plasma in atmosphere, such as nitrogen or hydrogen, using the material which contained the catalyst element as an electrode in an parallel monotonous type or positive column type plasma CVD equipment. However, the direction of an effect at the time of forming the thin film of oxidation silicon on this substrate, and forming a minute amount nickel thin film on it is more remarkable, when forming a nickel thin film [minute amount / on a substrate] rather than it forms a nickel thin film / minute amount / from 7059 glass substrates / directly /. As thinking as this reason, it is important for this low-temperature crystallization that silicon and nickel touch directly, and, in the case of 7059 glass, it is mentioned whether components other than silicon check contact or reaction of these both.

[0018] Moreover, even if it adds nickel with an ion implantation besides forming a thin film in contact with an amorphous silicon top or the bottom as the method of minute amount addition, the almost same effect is checked. the amount of nickel -- 1×10^{15} atoms/cm³ although low temperature-ization is checked in addition of the above amount -- 1×10^{21} atoms/cm³ the above addition -- setting -- Raman -- a spectrum -- the configuration of the peak of a spectrum is actually usable from differing from the object of a silicon simple substance clearly -- 1×10^{15} atoms/cm³ - 5×10^{19} atoms/cm³ It is thought that it is a range. Moreover, it is this amount when it considers using it for the barrier layer of TFT as semiconductor physical properties 1×10^{15} atoms/cm³ - 1×10^{19} atoms/cm³ To stop is required. However, that the above elements exist so much in a semiconductor checks the reliability and electric stability of equipment which used these semiconductors, and it is not a desirable thing.

[0019] That is, although the element (the element which promotes crystallization is called catalyst element on these specifications) which promotes crystallization of the above-mentioned nickel etc. is required in case it crystallizes amorphous silicon, it is desirable to make it not contained as much as possible in the crystallized silicon. In order to attain this purpose, while choosing a thing with the strong inclination for it to be inactive in crystalline silicon as a catalyst element, it is necessary to lessen the amount of a catalyst element required for crystallization as much as possible, and to crystallize in a minimum amount. About this amount, it has become clear that a bad influence arises in a device property that the nickel concentration in a barrier layer is not less than [1×10^{19} atoms cm⁻³]. And for that, it is necessary to control the addition of the above-mentioned catalyst element precisely, and to introduce it.

[0020] Moreover, the following matters became clear, when nickel was used as a catalyst element, the amorphous silicon film was formed, nickel addition was performed by the plasma treatment method, the crystalline silicon film was produced and the crystallization process etc. was examined in detail.

(1) When nickel is introduced on an amorphous silicon film by plasma treatment, before heat-treating, nickel has already invaded to the portion of the remarkable depth in an amorphous silicon film.

(2) The initial karyogenesis of a crystal is generated from the front face which introduced nickel.

(3) Even if it is the case where nickel is formed on an amorphous silicon film by the vacuum deposition, crystallization as well as the case where plasma treatment is performed takes place.

[0021] It comes to a conclusion that all the nickel introduced by plasma treatment is not functioning effectively from the above-mentioned matter. That is, it is thought that the nickel which is not fully functioning even if a lot of nickel is introduced exists. It is thought that it is functioning from this in case the point (field) that nickel and silicon have touched is low-temperature crystallization. And it concludes nickel that it is required to distribute in the shape of an atom minutely as much as possible. That is, "near the front face of an amorphous silicon film, within limits with low-temperature crystallization possible in which, as much as possible, low-concentration nickel distributes by the shape of an atom, and required one should just be introduced" comes to a conclusion.

[0022] Although a vacuum deposition can be mentioned as the method of introducing the nickel of a ultralow volume only near the front face of an amorphous silicon film, and a method of carrying out ultralow-volume introduction of the catalyst element which promotes crystallization only near the front face of an amorphous silicon film if it puts in another way, the controllability of a vacuum deposition is bad and it has the problem that it is difficult to control the amount of introduction of a catalyst element strictly.

[0023] Moreover, the problem from which crystallinity becomes poor in this case although a few thing is needed arises as much as possible, and control of a suitable quantity of a catalyst element is important for the amount of introduction of a catalyst element. Although this invention people invented the addition method of the catalyst element using the solution as a means to solve these, about this, it omits for details in this specification. By using this method, it has become clear for the concentration of a catalyst element to be controlled within the limits of 1×10^{16} atoms cm⁻³ - 1×10^{19} atoms cm⁻³. moreover, it has become clear that it is possible to use a kind or two or more kinds of elements which were chosen from Pd, Pt, Cu, Ag, Au, In, Sn, Pb, As, and Sb as a catalyst element with which the effect that it is the same besides nickel is acquired by research which are artificers

[0024] Then, the crystal growth at the time of performing nickel minute amount addition and the special feature of a crystalline form are described, and explanation is added about the crystallization mechanism guessed from there.

[0025] In not adding nickel as above-mentioned, a nucleus occurs at random from crystalline nuclei, such as a substrate interface, and if the crystal growth from the nucleus is random similarly and is depended on the production method (110) (111), it is reported that the crystal which carried out orientation comparatively is obtained, and though natural, an almost uniform crystal growth is observed over the whole thin film.

[0026] Analysis by DSC (differential scanning calorimeter) was performed that this mechanism should be checked first. While it had been attached to the substrate, the specimen container was filled up with the amorphous silicon thin film which formed membranes on the substrate by plasma CVD, and it carried out the temperature up by constant speed. Then, the clear exoergic

peak was observed before and after about 700 degrees C, and crystallization was observed. Although this temperature was naturally shifted when the programming rate was changed, when it carried out, for example at the rate of 10 degrees C/min, crystallization began from 700.9 degrees C. Next, what changed three kinds of programming rates was measured, and the activation energy of the crystal growth after initial nucleation was searched for by the Ozawa method from them. Then, the value of about 3.04eV was acquired. Moreover, when the rate equation was searched for from fitting with a theoretical curve, being explained best became clear with a disorderly nucleation and its growth model, the nucleus occurred at random from crystalline nuclei, such as a substrate interface, and the validity of a model called the crystal growth from the nucleus was checked.

[0027] The completely same measurement as the above-mentioned was performed also about what carried out minute amount addition of the nickel. Then, the activation energy of the crystal growth for which crystallization started from 619.9 degrees C when a temperature up was performed at the rate of 10 degrees C/min, and it asked from measurement of these series is about 1.87eV, and, also numerically, it became clear for a crystal growth to be easy. Moreover, it was suggested that the rate equation searched for from fitting with a theoretical curve has near to the model of single dimension-interface rate controlling, and has the directivity of the fixed direction in a crystal growth.

[0028] The data obtained by the above-mentioned thermal analysis are shown in the following table 5.

[0029] The activation energy shown in this table 5 is the stage of heating the sample, measures the heating value emitted from a sample, and computes it by the analysis means called Ozawa method from the result.

[0030]

[Table 5]

結晶化率	活性化エネルギー (eV)	
	ニッケル添加	ニッケル無添加
10%	2.04	2.69
30%	1.87	2.90
50%	1.82	3.06
70%	1.81	3.21
90%	1.83	3.34
平均	1.87	3.04

[0031] The activation energy in the above-mentioned table 5 is a parameter which shows the ease of carrying out of crystallization, and it is shown that are hard to carry out crystallization, so that the value is large, and it is easy to carry out crystallization, so that the value is small. If Table 5 is seen, the sample of nickel addition can grasp falling activation energy as crystallization progresses. That is, the bird clapper is shown that it is easier to perform crystallization as crystallization progresses. On the other hand, in the case of the crystalline silicon film by the nickel additive-free conventional method, activation energy is high and the bird clapper is shown as crystallization advances. This shows the bird clapper that it is harder to crystallize as crystallization advances. Moreover, if the average of activation energy is compared, the value of the silicon film crystallized by nickel addition will be about 62% in the case of a nickel additive-free crystalline silicon film, and the ease of carrying out of crystallization of the amorphous silicon film of the nickel addition also from this will be suggested.

[0032] Next, the result observed by transverse electromagnetic (transmission electron microscope) at the time of using 800A amorphous silicon as a start film about a crystalline form although nickel minute amount addition was carried out which is this time is shown. It is mentioned that a crystal growth differs from the field which added nickel in the portion of the near as a characteristic phenomenon made clear from the result of transverse-electromagnetic observation. That is, the stripes which will be believed to be moire or a lattice image if it observes from a cross section about the field which added nickel are mostly observed by the substrate at a perpendicular, a compound with the added nickel or its silicon serves as a crystalline nucleus, and this is mostly considered that it is shown that a crystal grows at a perpendicular by the substrate like what has not added nickel. Moreover, in the field of the circumference which added nickel, signs that the crystal growth was carried out in the direction parallel to a substrate needlelike or pillar-shaped were observed.

[0033] Although it is the foundation of a crystallography when explaining these phenomena still in detail, it will explain using the following signs. It is the sign which indicates a thing including all the fields equivalent to a field (hkl) to be {hkl} first. Moreover, it is the sign which indicates a thing including all shafts equivalent to the [hkl] shaft to be <hkl> similarly.

[0034] The observation result of the crystalline form near the field which added nickel is shown. First, although it was unexpected that the field which has not carried out direct minute amount addition of the nickel crystallized itself A nickel minute amount addition portion, the crystal-growth portion of the longitudinal direction of the near (it abbreviates to a part for a horizontal growing region henceforth), Furthermore, a distant amorphous portion (low-temperature crystallization is not performed in the portion left considerably) an amorphous portion remains ***** -- the concentration of nickel -- SIMS (secondary ion mass spectrometry) As shown in the place and drawing 17 which were investigated, concentration with the amount of horizontal growing region few from a nickel minute amount addition portion was detected, and as for the amorphous portion, the amount still fewer about 1 figure was observed. That is, nickel is considerably diffused over a large area and it is thought that crystallization of

the field near the field which added nickel is also the effect of nickel minute amount addition.

[0035] First, the surface transverse-electromagnetic image near the field which added nickel is shown in drawing 13 using 800A amorphous silicon. The needlelike or pillar-shaped crystal to which characteristic width of face was equal is observed by the substrate at an outline parallel direction so that more clearly than drawing. moreover, it observes that there is a layer in which contrast differs from other crystal portions in a part for the point of the crystal -- having -- the subsequent high resolution transverse electromagnetic and the result of transverse electromagnetic-EDX to this portion -- NiSi₂ it is -- the direction of crystal growth -- receiving -- perpendicular -- NiSi₂ What the layer exists (this is explained in full detail a back forge fire although this changes by thickness) has become clear. this substrate -- an outline -- from the field which carried out minute amount addition of the nickel, by the large thing, it was observed that hundreds of micrometers also grow and parallel horizontal growth found an increase and temperature of time also for amount of growth increasing proportionally becoming high As an example, growth of about about 20 micrometers was observed in 550 degrees C and 4 hours. subsequently, the above -- the TED pattern (electron-diffraction image) about three fields which carried out the crystal growth needlelike or pillar-shaped is shown in drawing 14 This TED pattern is taken from a direction perpendicular to a substrate. This pattern shows the crystal structure of a silicon film. When this pattern is seen, a pattern is very simple and it turns out that crystal orientation has gathered very much by the single crystal or the grade as which a thing like twin crystal is regarded even if many. As for the crystal which carried out horizontal growth from this pattern, using a 800 above-mentionedA amorphous silicon film as a start film, it turns out that the shaft orientations are the $\langle 111 \rangle$ directions. This relation is shown in drawing 16.

[0036] Based on the above experiment fact, artificers think that crystallization advances according to the following mechanisms.

[0037] If longitudinal growth is considered first, although karyogenesis will happen in the initial stage of crystallization, the activation energy in this case is reduced by minute amount addition of nickel. from [that crystallization has occurred from low temperature more when this adds nickel] -- obvious -- it is -- as this reason, it is thought that it is acting as a crystalline nucleus since one (NiSi₂) which it is among the intermetallic compounds which consist of nickel generated at low temperature and silicon has crystal silicon and the near lattice constant rather than amorphous silicon crystallizes besides the effect as a foreign matter of nickel Moreover, since this karyogenesis is generated almost simultaneous about the whole field surface which nickel added, a crystal growth serves as the mechanism in which it grows up with a field, as a result, a rate equation serves as a single dimension-interface rate-determining process in this case, and the crystal which carried out the crystal growth to the substrate at the outline perpendicular direction is obtained. however -- if it has the crystallographic axis which gathered completely under the influence of being restricted to thickness, stress, etc. -- ***** -- it does not go

[0038] However, when the pillar-shaped or needlelike crystal used the nickel addition portion as the nucleus, and it is equal to a longitudinal direction horizontally, since it is homogeneous as compared with a perpendicular direction, and it grows, and the direction of the growth side is set to $\langle 111 \rangle$, for example, a 800A amorphous silicon film is used for a substrate, the direction of a crystal growth is similarly set to $\langle 111 \rangle$. Of course, as for a rate equation, a single dimension interface rate-limiting type and a bird clapper are expected also in this case. since the activation energy of a crystal growth is reduced by adding nickel as above-mentioned, a very quick thing expects the growth rate of this longitudinal direction -- having -- the fact -- it is right [that]

[0039] Next, the electrical property about a part for the above-mentioned nickel minute amount addition portion and the horizontal growing region of the near is explained. The electrical property of a nickel minute amount addition portion is the addition of nickel as mentioned above, when it is a value of the same grade as the film which has not added nickel mostly about conductivity, i.e., the thing which performed crystallization at about 600 degrees C for dozens hours, and activation energy was searched for from the temperature dependence of conductivity 1017 atoms/cm³ - 1018 atoms/cm³ When it considered as a grade, behavior which is considered to originate in the level of nickel was not observed. That is, from this experiment fact, if it is the above-mentioned concentration, it will be considered that it can be used as a barrier layer of TFT etc.

[0040] The amount of horizontal growing region had the value high [as compared with a nickel minute amount addition portion / 1 or more figures] conductivity and quite high as a silicon semiconductor which has crystallinity to it. The grain boundary which exists while an electron passes by inter-electrode, since the path direction of current agreed with the horizontal growth direction of a crystal is considered [which there was or was almost] to depend especially, and this' corresponds without the result of a transparency electron ray microphotography, and conflict. [little] That is, since movement of a carrier becomes a thing in alignment with the grain boundary of the crystal which grew needlelike or pillar-shaped, it is possible that the state of being easy to move a carrier is realized.

[0041] Moreover, the transverse-electromagnetic photograph which is a photograph in which the crystal structure of the silicon to which the point which is shown in above-mentioned drawing 13, and which carried out the crystal growth needlelike or pillar-shaped was expanded is shown is shown in drawing 15. the black portion at the edge to drawing 15 -- appearing -- **** -- the passage of the above-mentioned [this portion] -- NiSi₂ it is -- things have become clear That is, nickel exists in the point of the crystal which carries out a crystal growth to a substrate needlelike in parallel or pillar-shaped intensively, and it is understood in the staging area that nickel concentration is low.

[0042] then, as one of the effect of the inventions indicated on these specifications, raising the mobility which is a carrier is mentioned to the above-mentioned grain boundary by carrying out outline coincidence of the outline ***** direction and the direction to which the carrier in a semiconductor device (for example, TFT) moves Moreover, while using the crystalline silicon film which a carrier tends to move by avoiding the point of the field which carried out the crystal growth in the direction parallel to a substrate, and using the staging area, i.e., the middle field of the field where the growth edge and nickel of the crystalline silicon film which carried out the crystal growth to the longitudinal direction were added, the composition using the low field of the concentration of nickel can be mentioned.

[0043] It is the growth direction which carried out the crystal growth needlelike [the direction in alignment with this grain boundary], or pillar-shaped. moreover, this growth direction It is the direction which has crystallinity in 800A thickness in the shaft orientations of <(the same thing has become clear in the thickness beyond this correctly)111>. further again this direction It is the direction which has high conductivity alternatively to other directions (for example, direction perpendicular to a crystal growth) as mentioned above. Moreover, it is difficult for the direction of a crystal growth and the direction where a carrier flows to be completely in agreement as an actual problem, and a crystal is also completely crossed to the whole surface, and it does not gather in the uniform direction and does not necessarily grow up. Then, as a practical question, the direction of a crystal growth is appointed as an average direction. Moreover, when we decide to consider that it is in agreement if the range of the direction and direction where a carrier flows is about **20 degrees and a 800A amorphous silicon film is used, going into this range completely has become clear.

[0044] Next, the control method of particle size and a stacking tendency is explained. Although the X diffraction was performed about the sample which crystallized by introducing a catalyst element, the following contents were examined as a parameter on that occasion.

[0045] - The field which added the comparison and the catalyst the case where a catalyst element is introduced into the front face of an amorphous silicon thin film, and at the time of introducing into an interface with a ground (it writes in longitudinal growth and this specification), By the case where the dependency and horizontal growth process when changing the dependency and catalyst concentration when changing the thickness of the comparison and the amorphous silicon film of the horizontal growth field of the circumference of it are used Comparison of whether this horizontal growth field considers as the structure where the upper and lower sides were inserted with oxidization silicon, or the upper surface considers as structure without oxidization silicon [0046] And an orientation ratio will be defined, as it is shown in the one following (111), in order to evaluate the acquired inclination quantitatively, when changing the above-mentioned parameter. (111) The above-mentioned (111) orientation ratio is the standard that a stacking tendency is high 0.67 (an orientation ratio is set to 0.33 if the above-mentioned definition is followed in completely random powder (111)) or more Although it was called orientation when there was a ratio of the double not less of this ratio (111), it decided to suppose that it is because it thought that it was satisfactory.

[0047]

[Equation 1]

(1 1 1) 配向存在比 = 1 (一定)

$$(2 2 0) \text{ 配向存在比} = \frac{\text{試料の (2 2 0) の (1 1 1) に対する相対強度}}{\text{粉末の (2 2 0) の (1 1 1) に対する相対強度}}$$

$$(3 1 1) \text{ 配向存在比} = \frac{\text{試料の (3 1 1) の (1 1 1) に対する相対強度}}{\text{粉末の (3 1 1) の (1 1 1) に対する相対強度}}$$

(1 1 1) 配向比率 =

$$\frac{(1 1 1) \text{ 配向存在比}}{(1 1 1) \text{ 配向存在比} + (2 2 0) \text{ 配向存在比} + (3 1 1) \text{ 配向存在比}}$$

[0048] And as a result of evaluating based on this (111) orientation ratio, the following table 1, Table 2, Table 3, Table 4, and an inclination like drawing 1 were observed.

[0049]

[Table 1]

触媒添加場所	配向性	粒径
シリコン表面	比較的ランダム	均一
下地界面	強く (1 1 1)	均一

[0050]

[Table 2]

成長方法	配向性	粒径
縦成長	比較的ランダム	均一
横成長	強く (111)	均一

[0051]

[Table 3]

薄い ← 膜厚 → 厚い
大 ← (111) 配向性 → 小

[0052]

[Table 4]

上面酸化膜の有無	配向性
酸化膜有り	概略 (111)
酸化膜無し	膜厚により変化

[0053] In addition, the production method is the same except [all] the parameter shown in front Naka, and especially the addition method used the longitudinal growth at the time of applying to a silicon front face about what is not indicated to be horizontal growth using the nickel addition method (it abbreviating to a liquid phase process henceforth) from a solution, using nickel as a catalyst element. However, in the horizontal growth process, in the experiment which compares the existence of an oxidation silicon film on top, in order to realize the horizontal growth process which does not have oxidation silicon in the upper surface, contrary to other horizontal growth processes, it left OCD only to the direct addition field (longitudinal-growth field) using what added nickel in the solution for SOG, such as OCD, and it considered as the structure where of no oxidation silicon is, on the field which should carry out horizontal growth. moreover, solid phase growth (SPC is written all over drawing) -- laser crystallization (by carrying out auxiliary, it is possible to raise crystallinity by leaps and bounds) of 550-degree-C 8 hours and after that -- 300 mJ/cm2 ** -- it carried out

[0054] Table 1 is a result at the time of changing a catalyst addition place as shown in front Naka, and the specific inclination for stacking tendencies to completely differ only by addition places differing was observed. In particle size, when most dependencies of an addition place were not observed but the particle size distribution was measured about arbitrary places, the width of face of a distribution is a half grade at the time of not adding a catalyst element, and it became clear that a uniform particle size is obtained.

[0055] Table 2 is a result at the time of changing the crystal-growth method, and is comparison with the portion to which the aperture which forms oxidation silicon on an amorphous silicon (covering oxidation silicon), carries out patterning of this oxidation silicon to the case (longitudinal growth) where nickel is introduced into the whole surface, and adds a catalyst element was opened in, and horizontal growth from there was carried out. Consequently, the longitudinal-growth portion was comparatively random, and although based also on thickness by the amount of [which has an oxidation silicon film in the upper surface] horizontal growing region (it mentions later about a thickness dependency), it had the stacking tendency nearly completely (111).

[0056] Although Table 3 was about the thickness dependency, the inclination for a stacking tendency to come out strongly was clearly checked, so that thickness was thin about a part for a horizontal growing region (111), when thickness experimented about 300 to 5000Å. Among this, as 400 to 800Å was shown in drawing 9, linearity was mostly found out within error range. In addition, about the longitudinal-growth portion, since it was ** random from the first, the clear inclination was not observed. Although Table 4 is in a horizontal growth process as a result of the experiment which compares the existence of an oxidation silicon film on top As opposed to all showing orientation other than a stacking tendency (111), as for the sample of the horizontal growth process which does not have oxidation silicon in the upper surface, although the stacking tendency changes with thickness It is as above-mentioned that the stacking tendency of the crystalline silicon obtained in a horizontal growth process in case there is oxidation silicon on top is quite strong (111) orientation in 800Å or less as a stacking tendency (111) is strong and it is suggested strongly also especially from drawing 9. And from this, it comes to a conclusion by making thickness into 800Å or

less that orientation (111) can be strengthened.

[0057] Although drawing 1 plots the dependency at the time of changing the addition of nickel using longitudinal growth, a horizontal axis shows the ratio of the area in which the right-hand side vertical axis is crystallizing [the left-hand side vertical axis] the orientation (111) ratio for the dose at the time of performing liquid phase addition using the acetate or the nitrate of nickel by solid phase growth among the silicon films before laser crystallization again. From this drawing, it is understood that it is possible to change an orientation (111) ratio freely to a random shell (111) stacking tendency with the concentration of a catalyst element. Moreover, it turns out that these are completely in agreement with change of a rate which grew by solid phase growth before laser crystallization, and even if that changed the rate which changed heating temperature and heating time instead of concentration change, and grew by solid phase growth before laser crystallization, it was checked by seeing the same inclination.

[0058] Next, although not shown in drawing, when particle size was shown, taking the particle size (it necessarily not being made clear whether the inside of this is a single crystal the place by present.) observed from the optical microscope for increasing a dose, and decreasing from 33 micrometers to 20 micrometers was checked.

[0059] Although it is on what mechanism the above-mentioned experimental result is based, about a stacking tendency, it is possible to interpret all by how much it was influenced of the silicon - oxidation silicon interface on the occasion of solid phase growth. It is as follows when the above-mentioned phenomenon is interpreted from such a viewpoint.

[0060] About the result of Table 1, when a catalyst element is introduced into a ground interface, in case karyogenesis is carried out, it is already influenced of the ground, and possibility of becoming a stacking tendency (111) at this time is high. As compared with it, when carrying out karyogenesis on a front face, random karyogenesis can be carried out, without being influenced of a ground. And it is thought throughout a crystal growth that it has the history.

[0061] A longitudinal-growth portion is the same mechanism as ****, and the result of Table 2 is considered these to be easy to be influenced greatly, in order to grow up about horizontal growth, while a growing point contacts a ground and the oxidation silicon of covering.

[0062] The ratio of the energy of an interface with the ground oxidation silicon to the free energy of the whole system will fall relatively, and the thickness dependency of Table 3 will be considered for the force which carries out orientation to (111) to become weaker, if thickness becomes thick.

[0063] About the result of two horizontal growth (what has an oxidation silicon film in the upper surface, and thing which is not) of Table 4, that by which the upper surface was being worn with oxidation silicon will be surrounded with oxidation silicon in the upper and lower sides as a result, and is considered to become a stacking tendency (111) that the interface should be stabilized. It is thought that restraint becomes weaker so much (111) and the horizontal growth process which does not have oxidation silicon in the upper surface shows the stacking tendency of an except to it since contribution of this interface becomes half. By the way, the upper surface had clear correlation between thickness and the stacking tendency in the horizontal growth process without oxidation silicon as mentioned above. For example, when 500A amorphous silicon was used (200) (311), the stacking tendency was observed strongly. This can be considered that the crystal growth has happened by mechanism like drawing 19 from crystallography-analysis and a photograph as shown in drawing 18. That is, the crystal-growth side 501 or 506 is a field (111), and although this is always fixed, in what angle this field has to the substrate, the thickness determines almost uniquely. If thickness changes as a result, for example in 800A thickness, the apparent direction 504 of a crystal growth and the crystal-growth side 501 will be almost perpendicular, and, as a result, a direction perpendicular to <111> shafts as a stacking tendency (when it is called a stacking tendency, generally a vertical stacking tendency is told to a substrate) will be observed. However, in 500A of thickness, it sees with the crystal-growth side 506, and the upper direction 505 of a crystal growth is not perpendicular, and, for the reason, a stacking tendency also changes. That is, in the horizontal growth process which does not have oxidation silicon in the upper surface, stacking-tendency control is possible by changing thickness. Above-mentioned longitudinal growth adds the result of drawing 1 to a random reason, and it is easily explained by admitting that laser crystallization is orientation (111). It is drawing 2 which showed the mechanism briefly. It is an example with many [A in drawing has few doses of a catalyst element, has few random portions currently crystallized by solid phase growth before laser crystallization, and] portions of the stacking tendency (111) which carried out laser crystallization rather than it, and B in drawing is that in which most carried out solid phase growth, and is an example which does not almost have the portion of the orientation (111) which carried out laser crystallization. The experiment to which the energy density and irradiation time in the case of laser crystallization were changed as an experiment which supports this was conducted. Then, it was made to take for an energy density and irradiation time to increase, and an orientation (111) ratio is high and the bird clapper became clear. This result is considered that being directly linked with raising the rate crystallized with laser raising an orientation (111) ratio is shown.

[0064] Next, in order to explain the above-mentioned phenomenon about particle size, when a catalyst element is used, it does not call at the addition place etc., but karyogenesis density is uniquely determined by the dose of a catalyst element, and if it thinks that the size which can carry out a crystal growth as a result will be decided, it can explain.

[0065] Therefore, when these are summarized, low-temperature crystallization and the control method of a stacking tendency are as follows.

[0066] For crystallization, solid phase growth and laser crystallization will be used together using the method of adding the catalyst element first represented by nickel as a premise by the liquid phase process from a front face. Thus, low-temperature-izing of crystallization temperature and fast shortening of the time to require are attained by adding a catalyst element in a minute amount.

[0067] *(111) When a stacking tendency wants to obtain a high film, make the crystallization ratio before laser crystallization small, using a horizontal growth process. By using this method, it is possible to control an orientation (111) ratio arbitrarily

between 0.67-1. What is necessary is just to choose either of the methods which makes the dose of a catalyst element small or changes solid phase growth conditions as a method of lowering this crystallization ratio.

[0068] - Enlarge the crystallization ratio before laser crystallization using a longitudinal-growth process to obtain a random film. What is necessary is just to choose either of the methods which makes [many] the dose of a catalyst element or changes solid phase growth conditions as a method of raising this crystallization ratio.

[0069] - Make the crystallization ratio before laser crystallization suitable using a longitudinal-growth process to obtain the film which has the above-mentioned middle stacking tendency. By using this process, it is possible to control an orientation (111) ratio arbitrarily between 0.33-1. What is necessary is to change the dose of a catalyst element or just to choose either of the methods which changes solid phase growth conditions as a method of making this crystallization ratio a suitable value.

[0070] - Control a stacking tendency by changing thickness to the upper surface using a horizontal growth process without oxidization silicon to obtain the film of other stacking tendencies. In this case, it says from a controllability and is desirable to make it change between 800A and about 300A as thickness. More than it, when thick, the width of face of a columnar crystal became small, and it was easy to change from thickness to a random inclination, and the crystal growth was difficult in 300A or less.

[0071] Next, what is necessary is just to perform it as follows as a means to change the particle size of a crystal.

- When enlarging particle size, lower the concentration of the catalyst element to add.

[0072] - When making particle size small, raise the concentration of the catalyst element to add.

[0073] In addition, as soon as ****(ing) controls the addition of the above-mentioned catalyst element, it is effective they. [the temperature and time of solid phase growth] However, it is uniquely determined by the addition of the aforementioned catalyst element to how much [maximum] particle size can be enlarged.

[0074] in this invention, although the most remarkable effect can be acquired when nickel is used as a catalyst element, in addition if it considers as the kind of catalyst element which can be used, Pt, Cu, Ag, Au, In, Sn, Pd, P, As, and Sb can be used preferably To silicon, these elements are invaded type elements, and are diffused in the silicon film, and it has the operation which promotes crystallization.

[0075] Moreover, the introductory method of a catalyst element is not limited to the liquid phase process which used solutions, such as solution and alcohol, and the matter containing the catalyst element can be widely used for it. For example, metallic compounds and the oxide containing the catalyst element can be used.

[0076] Then, how to apply to TFT, after being based on various above-mentioned properties is explained to the last. The active matrix type liquid crystal display which uses TFT for the drive of a pixel as an applicable field of TFT here shall be assumed. As mentioned above, in the active matrix type liquid crystal display of the latest big screen, although it is important to suppress the shrinkage of a glass substrate, by using the nickel minute amount addition process of this invention, as compared with the point distortion] of glass, it can fully crystallize at low temperature, and is especially suitable. If this invention is used, transposing to the silicon which has crystallinity is easily possible by carrying out minute amount addition of the nickel, and crystallizing the portion which used amorphous silicon conventionally at about 500-550 degrees C for about 4 hours. Of course, although it is necessary to change a design rule etc. into it suitability, equipment and a process can fully respond by the conventional object, and the merit is considered to be a large thing. Although the example of the TFT (TFT) which has an insulated-gate type in this specification is mainly shown, invention indicated on these specifications can be widely used for the element which used the thin film semiconductor. For example, it can use for thin film diode, a thin film bipolar transistor, and the photoelectrical inverter using the thin film semiconductor further.

[0077]

[Example]

[Example 1] this example is an example which prepares a 1200A oxidization silicon film alternatively, introduces nickel for this oxidization silicon film alternatively as a mask, is made to perform horizontal growth, and produces the high silicon film of a stacking tendency (111).

[0078] The outline of the production process in this example is shown in drawing 3 . First, the oxidization silicon film 21 (covering oxidization silicon) which serves as a mask on the amorphous silicon film 12 (500A film of plasma CVD) on a glass substrate 11 (Corning 7059, 10cm angle) is formed in thickness of 1200A 1000A or more and here. About the thickness of this oxidization silicon film 21, according to an artificer's etc. experiment, at least 500A of satisfactory things is checked, and if membranous quality is precise, it will be thought that it may be still thinner.

[0079] And according to the usual photograph RISOPA turning process, par NINGU of the oxidization silicon film 21 is carried out at the pattern to need. And the thin oxidization silicon film 20 is formed by irradiation of the ultraviolet rays in oxygen atmosphere. This oxidization silicon film improves wettability, and it is formed in order for the solution containing the nickel introduced behind to apply uniformly. Production of this oxidization silicon film 20 is performed by irradiating UV light for 5 minutes in oxygen atmosphere. In addition, the thickness of this oxidization silicon film 20 is considered to be about 20-50A.

(Drawing 3 (A))

[0080] In this state, 5ml dropping (in the case of 10cm angle substrate) of the acetate solution containing 100 ppm nickel is carried out. Moreover, 50rpm performs the spin coat for 10 seconds by the spinner 15, and the uniform water screen 14 is made to form in the whole substrate front face in this case. Furthermore, in this state, after holding for 1 minute, 2000rpm and spin-dry for 60 seconds are performed using a spinner. In addition, you may perform this maintenance, rotating 0 - 100rpm on a spinner.

(Drawing 3 (B))

[0081] And the amorphous silicon film 12 is crystallized by giving heat-treatment of 550 degrees (nitrogen-gas-atmosphere

mind) and 8 hours. Under the present circumstances, a crystal growth is performed in a longitudinal direction to the field which nickel was introduced and consisted of a field of a portion 22 where nickel was introduced as shown in 23. On condition that this time, about 30 micrometers was obtained as horizontal amount of growth. And covering oxidization silicon is exfoliated after that using buffer fluoric acid, and it is 300 mJ/cm². Laser crystallization by the KrF excimer laser (248nm) was performed with power density.

[0082] Thus, in the obtained silicon film, when the X diffraction was performed, the film with a very high stacking tendency 0.917 and a stacking tendency (111) orientation (111) ratio was obtained. The result is shown in drawing 4.

[0083] [Example 2] this example is an example which tried only the thickness of an amorphous silicon film on two kinds, 400A and 800A, using the completely same process as an example 1.

[0084] As a result, it is nearly completely [ratio / orientation (111) / for which it asked from the X diffraction / a 400A sample / as about 1.0] (111) the film of orientation, and it made the 800A sample clear that the stacking tendency is weak a little (111) as compared with 0.720 and 500A.

[0085] [Example 3] In this example, it is the example which solution is made to contain the catalyst element which promotes crystallization, it applies on an amorphous silicon film, and after an appropriate time is crystallized by heating, and raises crystallinity by irradiation of a laser beam further. This composition can obtain the film which has a comparatively random stacking tendency in longitudinal growth in the above-mentioned publication.

[0086] Even the place which introduces a catalyst element (here, nickel is used) is explained using drawing 5. In this example, Corning 7059 glass is used as a substrate 11. Moreover, the size is set to 100mmx100mm.

[0087] First, 100-1500A of amorphous silicon films 12 is formed by the plasma CVD method or the LPCVD method. Here, the amorphous silicon film 12 is formed in thickness of 500A by the plasma CVD method. (Drawing 5 (A))

[0088] And in order to remove dirt and a natural oxidation film, fluoric acid processing is performed, and an oxide film 13 is formed to 10-50A after that. What is necessary is just to use a natural oxidation film as it is instead of an oxide film 13, when dirt can be disregarded.

[0089] In addition, although exact thickness is unknown since this oxide film 13 is ultra-thin, it is thought that it is about 20A. Here, an oxide film 13 is formed by irradiation of UV light in the inside of oxygen atmosphere. Membrane formation conditions carried out UV to irradiating for 5 minutes later on into oxygen atmosphere. The thing using the oxidizing [thermally] method as the membrane formation method of this oxide film 13 is sufficient. Moreover, it may be based on processing by the hydrogen peroxide.

[0090] This oxide film 13 is the process which applies the acetate solution containing next nickel, and in order that it may spread an acetate solution round the whole front face of an amorphous silicon film, it is a thing for a wettability improvement. For example, since amorphous silicon flips an acetate solution when a direct acetate solution is applied to the front face of an amorphous silicon film, nickel cannot be introduced into the whole front face of an amorphous silicon film. That is, uniform crystallization cannot be performed.

[0091] Next, the acetate solution of nickel is made. Concentration of nickel is set to 25 ppm. And 2ml of this acetate solution is dropped at the front face of the oxide film 13 on the amorphous silicon film 12, and the water screen 14 is formed. Moreover, this state is held for 5 minutes. And spin-dry (2000rpm, 60 seconds) is performed using a spinner. (Drawing 5 (C), (D))

[0092] Although the concentration of the nickel in an acetic-acid solution was that it is used when it was 1 ppm or more, the example was taken with the desired stacking tendency and 25 ppm took this time. Moreover, when using the non-polar solvent like the toluene solution of 2-ethyl hexanoic-acid nickel as a solution, the oxide film 13 is unnecessary and can introduce a catalyst element on a direct amorphous silicon film.

[0093] The layer containing the nickel which has the thickness of a severalangstroms - hundreds of A average can be formed in the front face of the amorphous silicon film 12 after spin-dry by performing the application process of this nickel solution once to two or more times. In this case, in a subsequent heating process, the nickel of this layer is spread on an amorphous silicon film, and acts as a catalyst which promotes crystallization. In addition, this layer is not necessarily a perfect film. In addition, in this example, the number of times of an application could be 1 time.

[0094] The state is made to hold for 1 minute after the application of the above-mentioned solution. Although the concentration of the nickel finally contained in the silicon film 12 is controllable also by this time made to hold, the biggest controlling factor is the concentration of a solution.

[0095] And in a heating furnace, heat-treatment of 550 degrees and 8 hours is performed into nitrogen-gas-atmosphere mind. Consequently, the silicon thin film 12 which was formed on the substrate 11 and which has crystallinity in part can be obtained. It was 98.84% when asked for the crystallization ratio in this stage from the image analysis using the computer.

[0096] although the above-mentioned heat-treatment can be performed at the temperature of 450 degrees or more, heating time is made long if temperature is low -- if it kicks, it will not become but productive efficiency will fall. Moreover, if it is 550 degrees or more, the heat-resistant problem of the glass substrate used as a substrate will surface.

[0097] In this example, although how to introduce a catalyst element on an amorphous silicon film was shown, you may adopt the method of introducing a catalyst element into the bottom of an amorphous silicon film. However, it needs to be cautious of a stacking tendency becoming very high in that case as above-mentioned (111).

[0098] If the silicon film 12 which has crystallinity in part by heat-treatment is obtained, a KrF excimer laser (wavelength of 248nm, 30ns of pulse width) will be set in nitrogen-gas-atmosphere mind, and it is 200 - 350 mJ/cm². By number short-circuit and this example, one shot irradiates with power density at 300 mJ/cm², and the silicon film 12 is made to crystallize completely. This process is good also by irradiation of infrared light.

[0099] Thus, the X diffraction was performed for the silicon film which has the acquired crystallinity, and the stacking tendency was evaluated. The result is shown in drawing 6. (111) The peak was observed clearly, and was calculating an orientation ratio about this (111) with 0.405, and it became clear that it may be [a random film] as desired (311). (220)

[0100] [Example 4] this example sets to 1 ppm concentration of the nickel salt which is a catalyst element in an example 3. All other processings are the same as that of an example 3. By considering as such composition, it is possible to enlarge one diameter of crystal grain. Moreover, about this example, solid phase growth conditions were experimented on two conditions, the thing of 4 hours, and the object of 16 hours. As a result of carrying out microscope observation of the thin film after heat treatment, the sample which lowered concentration to this appearance and made time of solid phase growth 4 hours had more portions of amorphous silicon than the sample of an example 3, and the number of the crystalline nuclei which consist of crystalline silicon was also falling. Next, the sample after laser crystallization was observed by the SEKOETCHI back SEM. Consequently, it became clear by falling solution concentration like this time that it is possible to enlarge the size of one crystal grain as compared with the case of an example 2.

[0101] Furthermore, in the sample after laser crystallization, when the X diffraction was performed, as for the object of 4 hours, 0.730 and the film of a stacking tendency (111) were obtained [solid phase growth] for the orientation (111) ratio. Moreover, this orientation ratio was falling about to 0.4, and the film which performed solid phase growth for 16 hours had turned into a random film.

[Example 5] this example is an example which obtains TFT using the crystalline silicon film produced using the method of invention indicated on these specifications. TFT of this example can be used for active matrix type the driver line and pixel portion of a liquid crystal display. In addition, it cannot be overemphasized that it can use not only for a liquid crystal display but for the thin film integrated circuit generally said as an application range of TFT.

[0102] The outline of the production process of this example is shown in drawing 7. The oxidization silicon film (not shown) of a ground is first formed in thickness of 2000A on a glass substrate 11. This oxidization silicon film is prepared in order to prevent diffusion of the impurity from a glass substrate.

[0103] And an amorphous silicon film is formed in thickness of 500A by the same method as an example 1. And a thin oxide film is formed by irradiation of UV light in oxygen atmosphere in thickness of about 20A after the fluoric acid processing for removing a natural oxidation film. The method by filtered-water processing or thermal oxidation is sufficient as this thin production method of an oxide film.

[0104] And the acetate solution containing 25 ppm nickel is applied, it holds for 1 minute, and spin-dry is performed using a spinner. The oxidization silicon films 20 and 21 are removed by buffer fluoric acid after that, and a silicon film is crystallized by heating of 550 degrees and 8 hours. (It is the same as the production method shown in the example 1 so far)

[0105] By performing the above-mentioned heat-treatment, the silicon film with which the amorphous component and the crystal component were intermingled can be obtained. The crystalline nucleus exists in this crystal component. Furthermore at 200 - 300 mJ/cm² and this example, it is KrF excimer laser light 300 mJ/cm² The crystallinity of a silicon film is made to promote by irradiating. In the irradiation process of this laser beam, a substrate is heated at about 400 degrees C. this process -- crystallization is raised further

[0106] Next, patterning of the crystallized silicon film is carried out, and the island-like field 104 is formed. The field 104 of the shape of this island constitutes the barrier layer of TFT. And the 1000A oxidization silicon film 105 is formed 200-1500A in thickness, and here. This oxidization silicon film functions as a gate insulator layer. (Drawing 7 (A))

[0107] Cautions are required for production of the above-mentioned oxidization silicon film 105. Here, TEOS was used as the raw material, and with oxygen, the substrate temperature of 150-600 degrees C, it is 300-450 degrees C preferably, and decomposed and deposited by RF plasma CVD method. In the pressure ratio of TEOS and oxygen, 0.05 - 0.5torr and RF power set 1:1-1:3, and the pressure to 100-250W. Or 350-600 degrees C of substrate temperature were preferably formed as 400-550 degrees C by reduced pressure CVD or ordinary-pressure CVD with ozone gas by using TEOS as a raw material. It annealed at 400-600 degrees C by the atmosphere of oxygen or ozone after membrane formation for 30 to 60 minutes.

[0108] You may make crystallization of the silicon field 104 promote by irradiating a KrF excimer laser (wavelength of 248nm, 20ns of pulse width), or a strong light equivalent to it in this state. Since especially RTA (RAPITTO thermal annealing) using infrared light can heat only silicon alternatively and can moreover decrease the interface level in the interface of silicon and an oxidization silicon film, without heating a glass substrate, it is useful in production of an insulated-gate type electric field effect semiconductor device.

[0109] Then, an aluminum film with a thickness of 2000A - 1 micrometer is formed by the electron-beam-evaporation method, patterning of this is carried out and the gate electrode 106 is formed. To aluminum, you may dope a scandium (Sc) 0.15 to 0.2% of the weight. Next, anodic oxidation is performed, dipping a substrate in pH**7 and the ethylene glycol solution of 1 - 3% of tartaric acid, and using cathode and the gate electrode of this aluminum as an anode plate for platinum. Anodic oxidation raises voltage with fixed current to 220V at first, and it is held for 1 hour and it is made to end it in the state. In this example, the climbing speed of voltage has the amount of suitable 2-5v/in the state of a constant current. Thus, 1500-3500A in thickness and the 2000A anodic oxidation object 109 are formed. (Drawing 7 (B))

[0110] Then, an impurity (phosphorus) is poured into a self-adjustment target by using the gate polar zone as a mask into the island-like silicon film of each TFT by the ion doping method (it is also called the plasma doping method). A phosphoretted hydrogen (PH₃) is used as doping gas. A dose is set to 1-4x10¹⁵cm⁻².

[0111] Furthermore, as shown in drawing 7 (C), a KrF excimer laser (wavelength of 248nm, 20ns of pulse width) is irradiated, and the crystallinity of the portion into which crystallinity deteriorated by introduction of the above-mentioned impurity range is

made to improve. the energy density of laser -- 150 - 400 mJ/cm² -- desirable -- 200 - 250 mJ/cm² it is . In this way, the N type impurity (phosphorus) fields 108 and 109 are formed. Sheet resistance of these fields becomes 200-800ohms / **.

[0112] In this process, instead of using a laser beam, it is made to go up for a short time to 1000-1200 degrees C (a silicon monitor's temperature) using a flash lamp, and a sample is heated. You may use irradiation of strong light equivalent to the so-called laser beams, such as RTA (rapid thermal annealing) (it is also called RTP and a RAPITTO thermal process), here.

[0113] Then, an oxidization silicon film is formed in the whole surface 3000A in thickness by using TEOS as a raw material as a layer insulation object 110 by the plasma CVD method of this and oxygen, reduced pressure CVD with ozone, or ordinary-pressure CVD. Substrate temperature is made into 250-450 degrees C, for example, 350 degrees C. After membrane formation, in order to obtain surface flat nature, this oxidization silicon film is ground mechanically. (Drawing 7 (D))

[0114] And as it *****s and the layer insulation object 110 is shown in drawing 7 (E), a contact hole is formed in the source/drain of TFT, and the wiring 112 and 113 of chromium or a titanium nitride is formed.

[0115] Finally, it anneals at 300-400 degrees C in hydrogen for 0.1 to 2 hours, and hydrogenation of silicon is completed. Thus, TFT is completed. And TFT of a large number produced simultaneously is made to arrange in the shape of a matrix, and it completes as active matrix liquid crystal display. This TFT has the source / drain fields 108/109, and the channel formation field 114. Moreover, 115 becomes a part for the electric joint of NI.

[0116] It is thought that the concentration of the nickel which exists in a barrier layer is 1×10^{16} atoms cm⁻³ - 3×10^{18} atoms cm⁻³ about [3×10^{18} cm⁻³] 3 and not more than it when the composition of this example is adopted.

[0117] As for TFT produced by this example, the thing 75cm² / more than Vs is obtained for mobility by the N channel. Moreover, it is checked that Vth also has the small good property. Furthermore, it is checked that the variation in mobility is also less than **5%. Since the little of this variation has the random stacking tendency, it is thought that it is because there is no anisotropy in the operating characteristic of a device. Although the thing 100cm² / more than Vs can be easily obtained with an N channel type when only a laser beam is used, variation is large and cannot acquire homogeneity like this example.

[0118] [Example 6] this example is composition which sets nickel concentration of an example 5 to 1 ppm, and enlarges the diameter of crystal grain. The other composition is completely the same as that of an example 5.

[0119] As a result, the thing 150cm² / more than Vs was obtained for mobility by the N channel. It is thought that this is the effect to which the diameter of crystal grain became large. However, about **30% of variations of mobility existed, and homogeneity was not so high. Although this reason is not clear, since it has the stacking tendency (111) to some extent, it is surmised that the anisotropy may have arisen in the device.

[0120] [Example 7] In this example, as shown in an example 2, nickel is introduced alternatively, and the example which forms an electron device using the field which carried out the crystal growth to the longitudinal direction (direction parallel to a substrate) from the portion is shown. When such composition is adopted, nickel concentration in the barrier-layer field of a device can be made still lower, and it can consider as very desirable composition from the electric stability of a device, or reliability. Moreover, it is possible by making thickness of an amorphous silicon film into 400A to obtain the film of a stacking tendency nearly completely (111).

[0121] The production process of this example is shown in drawing 8 . First, a substrate 201 is washed and the ground film 202 of oxidization silicon with a thickness of 2000A is formed by the plasma CVD method by making TEOS (tetrapod ethoxy silane) and oxygen into material gas. And in 300-1500A in thickness, and this example, the 400A intrinsic (I type) amorphous silicon film 203 is formed by the plasma CVD method. Next, 500-2000A in thickness and the 1000A oxidization silicon film 205 are continuously formed by the plasma CVD method. And the oxidization silicon film 205 is *****ed alternatively and the field 206 which amorphous silicon exposed is formed.

[0122] And a solution (here acetate solution) application is carried out including the nickel element which is a catalyst element which promotes crystallization by the method shown in the example 2. The concentration of the nickel in an acetic-acid solution is 100 ppm. In addition, detailed process sequence and detailed conditions are the same as that of what was shown in the example 1. This process may be based on the method shown in the example 5 or the example 6.

[0123] Then, 500-620 degrees C, for example, 550 degrees C, and heating annealing of 8 hours are performed under nitrogen-gas-atmosphere mind, and the silicon film 203 is crystallized. Crystallization makes a starting point the field 206 where nickel and the silicon film contacted, and as shown by the arrow, a crystal growth advances in the parallel direction to a substrate. In drawing, as for a field 204, nickel shows the portion which it was directly introduced and was crystallized, and the portion which crystallized the field 203 in the longitudinal direction. The crystal to the longitudinal direction shown by this 203 is about 25 micrometers. (Drawing 8 (A))

[0124] The crystallinity of the silicon film 203 is made to promote by irradiation of a laser beam further after the crystallization process by the above-mentioned heat-treatment. This process is 350 mJ/cm² in a high energy and this example more nearly further than an example 1, in order to give laser crystallization, without removing the oxidization silicon film 205, although it is completely the same as that of an example 1. It crystallized.

[0125] Next, the oxidization silicon film 205 is removed. Under the present circumstances, the oxide film formed in the front face of a field 206 is also removed simultaneously. And dry etching of the silicon film 204 is carried out after patterning, and the island-like barrier-layer field 208 is formed. Under the present circumstances, nickel is the field introduced directly and the field shown by drawing 8 (A) 206 is a field where nickel exists in high concentration. Moreover, it is checked that nickel exists also at the nose of cam of a crystal growth too at high concentration. In these fields, it has become clear that the concentration of nickel is high as compared with the middle field. Therefore, it was made for the field where such nickel concentration is high not to lap with a channel formation field in a barrier layer 208 in this example.

[0126] Then, by (ten atmospheric pressure containing the steam of 100 volume %, and 500-600 degrees C) leaving it in 550-degree C atmosphere typically for 1 hour, the front face of a barrier layer (silicon film) 208 is oxidized, and the oxidization silicon film 209 is formed. Thickness of an oxidization silicon film is made into 1000A. After forming the oxidization silicon film 209 by thermal oxidation, a substrate is made to hold at ammonia atmosphere (one atmospheric pressure, 100%) and 400 degrees C. And the infrared light which has a peak in the wavelength of 0.6-4 micrometers, for example, 0.8-1.4 micrometers, to a substrate is irradiated for 30 to 180 seconds in this state, and nitriding treatment is performed to the oxidization silicon film 209. In addition, you may mix 0.1 - 10% of HCl in atmosphere in this case. (Drawing 8 (B))

[0127] Then, 3000-8000A in thickness and 6000A aluminum (0.01 - 0.2% of scandium is included) are formed by the sputtering method. And patterning of the aluminum film is carried out and the gate electrode 210 is formed. (Drawing 8 (C))

[0128] Furthermore, the front face of the electrode of this aluminum is anodized and an oxide layer 211 is formed in a front face. This anodic oxidation is performed in the ethylene glycol solution with which the tartaric acid was contained 1 to 5%. The thickness of the oxide layer 211 obtained is 2000A. In addition, since this oxide 211 serves as thickness which forms an offset gate field in a next ion doping process, the length of an offset gate field can be decided at the above-mentioned anodic oxidation process. (Drawing 8 (D))

[0129] next, the ion doping method (the plasma doping method may be used) -- a barrier-layer field (the source/drain, and a channel are constituted) -- the oxidizing zone 211 of the gate electrode section 210, i.e., a gate electrode, and its circumference -- a mask -- carrying out -- self -- the impurity (here phosphorus) which gives N conductivity type conformably is added. Acceleration voltage is made into 60-90kV, for example, 80kV, using a phosphoretted hydrogen (PH3) as doping gas. A dose carries out to 1×10^{15} - $8 \times 10^{15} \text{ cm}^{-2}$, $4 \times 10^{15} \text{ cm}^{-2}$ [for example,]. Consequently, the impurity ranges 212 and 213 of N type can be formed. An impurity range and a gate electrode will be in the offset state which only distance x left so that clearly from drawing. Such an offset state especially is effective when reducing the leakage current (it is also called the OFF state current) at the time of impressing reverse voltage (it subtracting in the case of N channel TFT) to a gate electrode. Since it is desired for a leakage current to be low so that the charge accumulated at the pixel electrode may not escape in order to acquire a good picture in TFT which controls the pixel of an active matrix like this example especially, it is effective to establish offset.

[0130] Then, irradiation of a laser beam performs annealing. As a laser beam, although a KrF excimer laser (wavelength of 248nm, 20ns of pulse width) is used, you may be other laser. For the irradiation conditions of a laser beam, an energy density is 200 - 400 mJ/cm², for example, 250 mJ/cm². It carried out and 2-10 shots per place irradiated two shots, for example. You may make an effect increase by heating a substrate at about 200-450 degrees C at the time of irradiation of this laser beam. (Drawing 8 (E))

[0131] Then, it forms by the plasma CVD method by using the oxidization silicon film 214 with a thickness of 6000A as a layer insulation object. Furthermore, by the spin coating method, the transparent polyimide film 215 is formed and flattening of the front face is carried out.

[0132] And a contact hole is formed in the layer insulation objects 214 and 215, and the electrode and the wiring 217 and 218 of TFT are formed by the multilayer of a metallic material, for example, a titanium nitride, and aluminum. Finally, 350 degrees C and annealing for 30 minutes are performed in the hydrogen atmosphere of one atmospheric pressure, and the pixel circuit of the active matrix which has TFT is completed. (Drawing 8 (F))

[0133] Since TFT produced by this example can obtain high mobility, it can use for the driver line of an active matrix type liquid crystal display. Specifically, the thing 250 cm^2 / more than Vs was obtained for mobility by the N channel. Since the stacking tendency of a crystal became very high, this is expected to originate in the potential barrier in a grain boundary having fallen.

[0134] [Example 8] this example changes the method of horizontal growth of an example 7 into the method which used OCD. namely, -- here [the SOG film and here] which 500-2000A in thickness which formed membranes continuously after the 500A intrinsic (I type) amorphous silicon film 203, and the 1000A oxidization silicon film 205 were omitted here, instead made nickel contain -- Tokyo -- OCD made from adaptation Type-2 Material of NONDO - PU The object which made the nickel compound contain in this was formed using Si-59000-SG. If membrane formation was preceded, the front face was exposed to ozone, the very thin oxide film was formed, and OCD was formed after that. PURIBE - KU (80 degrees C and 150 degrees C) was performed after that, and the 250-degree C cure was performed continuously. Since nickel will already be spread in amorphous silicon in this process if the temperature of this cure is too high, cautions are required. Moreover, since at least 250 degrees C of nickel fully diffuse the very thin oxide film generated by ozone when it acts as a barrier of the diffusion in this cure process and there is this [no], cautions are required. Next, predetermined patterning is performed. This patterning used what carried out positive negative reversal by the resist using the mask of an example 7. Since etching after patterning has the very early etching rate of OCD, its DOREI process is more desirable than a sentiment. Since it is almost the same as that of an example 7, the following processes are skipped. The property of obtained TFT was almost the same as that of the object of an example 7. When a part for GE - Urabe of obtained TFT was exfoliated and the stacking tendency of the barrier-layer portion under it was investigated from the electron diffraction, it was observed that it is orientation mostly (200).

[0135] [Example 9] this example is an example which forms the circuit which combined with the complementary type P channel type TFT (it is called PTFT) using the crystalline silicon film formed on the glass substrate, and N channel type TFT (it is called NTFT). The composition of this example can be used for a switching element, a peripheral-driver circuit, and also active type image sensors and the integrated circuit of a pixel electrode of a liquid crystal display. The cross section of the production process of this example is shown in drawing 10. First, the ground film 302 of oxidization silicon with a thickness of 2000A is formed by the sputtering method on a substrate (Corning 7059) 301. The mask 303 formed with the metal mask or the oxidization silicon film next is formed. This mask 303 makes the ground film 302 expose in the shape of a slit in the field of 300. Namely, if the state

of drawing 10 (A) is seen from the upper surface, the shape of a slit, the ground film 302 is exposed and other ***** are in the state where the mask is carried out.

[0136] After forming the above-mentioned mask 303, 5-200Å in thickness and a 20Å silicification nickel film (a chemical formula NiSi_x and $0.4 \leq x \leq 2.5$, for example, $x = 2.0$) are alternatively formed to the field of 300 by the sputtering method.

[0137] Next, 500-1500Å in thickness and the 1000Å intrinsic (I type) amorphous silicon film 304 are formed by the plasma CVD method. and this -- 550 degrees C or inert-atmosphere-izing (atmospheric pressure) under hydrogen-reduction atmosphere (the partial pressure of hydrogen is 0.1 to 1 atmospheric pressure preferably) -- it comes out, and it anneals for 4 hours and 550 degrees C is crystallized Under the present circumstances, in the field of 300 to which the silicification nickel film was formed alternatively, crystallization of the amorphous silicon film 304 takes place perpendicularly to a substrate 301. And in fields other than field 300, as an arrow 305 shows, a crystal growth is performed in a longitudinal direction (direction parallel to a substrate) from a field 300.

[0138] As a result of the above-mentioned process, the amorphous silicon film 304 can be crystallized and a crystalline silicon film can be obtained. Then, the oxidization silicon film 306 with a thickness of 1000Å is formed as a gate insulator layer by the sputtering method. Using oxidization silicon as a target, the substrate temperature at the time of sputtering is oxygen and an argon, and makes 200-400 degrees C, for example, 350 degrees C, and sputtering atmosphere at sputtering an argon / oxygen = 0-0.5 (0.1 or less [for example,]). And separation between elements is performed and the barrier-layer field of TFT is decided. Under the present circumstances, it is important to make it the point of a crystal growth shown by 305 not exist in the portion used as a channel formation field. The carrier which moves between the source/drain can be prevented from being influenced of a nickel element in a channel formation field by carrying out like this.

[0139] Then, 6000-8000Å in thickness and 6000Å aluminum (0.1 - 2% of silicon is included) are formed by the sputtering method.

[0140] And patterning of the aluminum film is carried out and the gate electrodes 307 and 309 are formed. Furthermore, the front face of the electrode of this aluminum is anodized and oxide layers 308 and 310 are formed in a front face. This anodic oxidation was performed in the ethylene glycol solution with which the tartaric acid was contained 1 to 5%. The thickness of the obtained oxide layers 308 and 310 was 2000Å. In addition, since these oxides 308 and 310 serve as thickness which forms an offset gate field in a next ion doping process, the length of an offset gate field can be decided at the above-mentioned anodic oxidation process.

[0141] Next, the impurity which gives one conductivity type to a barrier-layer field (the source/drain, and a channel are constituted) is added by IONDO pouring. In this doping process, an impurity (phosphorus and boron) is poured in by using the oxidizing zone 310 of the gate electrode 307, the oxidizing zone 308 of the circumference and the gate electrode 309, and its circumference as a mask. In the case of the former, in the case of 60-90kV, for example, 80kV, and the latter, acceleration voltage is made into 40-80kV, for example, 65kV, using a phosphoretted hydrogen (PH_3) and a diboron hexahydride (B_2H_6) as doping gas. The amount of DOSU sets 1×10^{15} - $8 \times 10^{15} \text{cm}^{-2}$, for example, phosphorus, to $2 \times 10^{15} \text{cm}^{-2}$, and sets boron to 5×10^{15} . On the occasion of doping, each element is alternatively doped by covering one field by the photoresist. Consequently, the impurity ranges 314 and 316 of N type and the impurity ranges 311 and 313 of P type are formed, and the field of the field of P channel type TFT (PTFT) and N channel type TFT (NTFT) can be formed.

[0142] Then, it is annealing **** by irradiation of a laser beam. As a laser beam, although the KrF excimer laser (wavelength of 248nm, 20ns of pulse width) was used, you may be other laser. For the irradiation conditions of a laser beam, an energy density is 200 - 400 mJ/cm², for example, 250 mJ/cm². It carries out and 2-10 shots per place irradiate two shots, for example. It is useful to heat a substrate at about 200-450 degrees C at the time of irradiation of this laser beam. Since nickel is spread in the field crystallized previously, the impurity ranges 311 and 313 by which the impurity which recrystallization advances easily and gives P type by irradiation of this laser beam was doped, and the impurity ranges 314 and 316 by which the impurity which gives N further was doped can make it easily activated in this laser annealing process.

[0143] The method by lamp annealing by infrared radiation (for example, 1.2 micrometers) is sufficient as this process. Infrared radiation is easy to be absorbed to silicon, and can perform effective annealing which is equal also to heat annealing of 1000 degrees or more. Since a glass substrate is not heated to an elevated temperature on the other hand since it is hard to be absorbed to a glass substrate, and it ends by short-time processing, it can be said that it is the optimal method in the process from which the shrinkage of a glass substrate poses a problem.

[0144] Then, it forms by the plasma CVD method by using the oxidization silicon film 318 with a thickness of 6000Å as a layer insulation object, a contact hole is formed in this, and the electrode and the wiring 317, 320, and 319 of TFT are formed by the multilayer of a metallic material, for example, a titanium nitride, and aluminum. Finally, 350 degrees C and annealing for 30 minutes were performed in the hydrogen atmosphere of one atmospheric pressure, and the semiconductor circuit which constituted TFT in the complementary type was completed. (Drawing 10 (D))

[0145] Although the circuit shown above is the CMOS structure which prepared PTFT and NTFT in the complementary type, it can also produce two independent TFT simultaneously by making two TFT simultaneously and cutting in the center in the above-mentioned process.

[0146] The outline which looked at drawing 10 (D) from the upper surface to drawing 11 is shown. The sign in drawing 11 corresponds to the sign of drawing 10. As shown in drawing 11, the direction of crystallization is a direction shown by the arrow, and the crystal growth is performed in the direction of the source / drain field (the direction of a line which connected the source field and the drain field). A carrier moves along with the crystal which grew needlelike or pillar-shaped between the source/drain at the time of operation of TFT of this composition. That is, a carrier moves along with the grain boundary of a needlelike or

pillar-shaped crystal. Therefore, the resistance received in case a carrier moves can be reduced, and TFT which has high mobility can be obtained.

[0147] In this example, although the method of forming nickel alternatively on the ground film 302 under the amorphous silicon film 304 as a method of introducing nickel as a thin film (it being difficult to observe as a film since it is very thin), and making it performing a crystal growth from this portion was adopted, the method of forming a silicification nickel film alternatively, after forming the amorphous silicon film 304 may be used. That is, a crystal growth may be performed from the upper surface of an amorphous silicon film, and may be performed from the undersurface. Moreover, an amorphous silicon film may be formed beforehand and the method of pouring in nickel ion alternatively into this amorphous silicon film 304 may be further adopted using the ion doping method. In this case, it has the feature that the concentration of a nickel element is controllable. Moreover, the method by plasma treatment or CVD is sufficient as the introductory means of nickel against an amorphous silicon film.

[0148] [Example 10] this example is an example prepared in each pixel by making N channel type TFT into a switching element in an active type liquid crystal display. Although one pixel is explained below, a pixel [a large number (generally hundreds of thousands) otherwise] is formed with the same structure. Moreover, it cannot be overemphasized that not an N channel type but a P channel type may be used. Moreover, it can use for image sensors or other equipments. That is, if it uses with thin film TORANJITA, especially the use will not be limited.

[0149] The outline of the production process of this example is shown in drawing 12. In this example, the Corning 7059 glass substrate (1.1mm in thickness, 300x400mm) was used as a substrate 401. First, the ground film 402 (oxidization silicon) is formed in the thickness of 2000A by the sputtering method. In order [this] to introduce nickel in post selection, a mask 403 is formed by the metal mask, the oxidization silicon film, or the photoresist. And a silicification nickel film is formed by the sputtering method. This silicification nickel film is formed in the thickness of 5-200A, for example, the thickness of 20A, by the sputtering method. This silicification nickel film is shown by the chemical formula NiSi_x and $0.4 \leq x \leq 2.5$, $x = 2.0$ [for example,]. Thus, a silicification nickel film is alternatively formed in a field 404.

[0150] Then, the amorphous silicon film 405 is formed in the thickness of 1000A by the LPCVD method or the plasma CVD method, and after performing dehydrogenation at 400 degrees C for 1 hour, it crystallizes by heating annealing. This annealing process was performed at 550 degrees C for 4 hours under hydrogen-reduction atmosphere (the partial pressure of hydrogen is 0.1 to 1 atmospheric pressure preferably). Moreover, you may perform this heating annealing process in inert atmospheres, such as nitrogen.

[0151] In this annealing process, since the silicification nickel film is formed in some fields under the amorphous silicon film 405, crystallization takes place from this portion. In the case of this crystallization, as the arrow of drawing 12 (B) shows, in the portion 404 in which silicification nickel is formed, the crystal growth of silicon advances perpendicularly to a substrate 401. Moreover, as similarly shown by the arrow, in the field (fields other than field 404) which silicification nickel is formed and is not, a crystal growth is performed in the parallel direction to a substrate.

[0152] In this way, the semiconductor film 405 which consists of crystalline silicon can be obtained. Next, patterning of the above-mentioned semiconductor film 405 is carried out, and an island-like semiconductor region (barrier layer of TFT) is formed. Under the present circumstances, it is important like an arrow to make it the point of the crystal which carried out the crystal growth not exist in a barrier layer, especially a channel formation field. Specifically, when the point of the arrow of drawing 12 (B) is a terminal point (edge) at a crystal growth, it is useful to use the interstitial segment which removed the crystalline silicon film 405 of the portion of 404 into which nickel was introduced, and the portion of the terminal point (drawing left end) of this arrow by etching, and carried out the crystal growth in the direction parallel to the substrate of the crystalline silicon film 405 as a barrier layer. This is for preventing the nickel concentrated on this point having a bad influence on the property of TFT based on the fact which nickel is concentrating on the crystal-growth point.

[0153] Furthermore, the gate insulator layer (70-120nm in thickness typically 100nm) 406 of oxidization silicon is formed by the plasma CVD method in oxygen atmosphere by using a tetrapod ethoxy silane (TEOS) as a raw material. In order to prevent the shrinkage and camber of glass, 400 degrees C or less of substrate temperature are preferably made into 200-350 degrees C.

[0154] Next, the gate electrode 407 is formed by forming the film which made well-known silicon the principal component by CVD, and performing patterning. Then, as an impurity of N type, Lynn is poured in with ion-implantation and the source field 408, the channel formation field 409, and the drain field 410 are formed in a self-adjustment target. And the crystallinity of the crystalline silicon film which deteriorated is made to improve by irradiating a KrF laser beam for an ion implantation. At this time, the energy density of a laser beam is 250 - 300 mJ/cm². It carries out. By this laser radiation, sheet resistance of the source/drain of this TFT is the 300 - 800 ohm/cm². It becomes. It is useful that lamp annealing of infrared radiation performs this annealing process.

[0155] Then, the layer insulation object 411 is formed with oxidization silicon, and the pixel electrode 412 is further formed by ITO. And a contact hole is formed, and electrodes 413 and 414 are formed in the source / drain field of TFT by chromium / aluminum multilayer, among these one electrode 414 is connected also to ITO412. Finally, it anneals at 200-300 degrees C in hydrogen for 2 hours, and hydrogenation of silicon is completed. Thus, TFT is completed. This process is simultaneously performed also in a majority of other pixel fields.

[0156] Since the crystalline silicon film made to carry out a crystal growth in the direction in which a carrier flows as a barrier layer which constitutes a source field, a channel formation field, and a drain field was used, a carrier would not cross the grain boundary, namely, a carrier would move along with the grain boundary of a needlelike or pillar-shaped crystal, TFT produced by this example was able to obtain TFT with the high mobility of a carrier. TFT produced by this example was an N channel type,

and the mobility was 90-130 (cm^2 / Vs). As compared with movements having been 80-100 (cm^2 / Vs) at N channel type TFT using the crystal silicon film obtained by crystallization by conventional 600 degrees C and heat annealing of 48 hours, this is improvement in the property that this is big.

[0157] Moreover, when P channel type TFT was produced and the mobility was measured by the same production method as the above-mentioned process, it was 50-80 (cm^2 / Vs). As compared with movements having been 30-60 (cm^2 / Vs) at P channel type TFT using the crystalline silicon film from which this was also obtained by crystallization by conventional 600 degrees C and heat annealing of 48 hours, it is improvement in a big property.

[0158] [Example 11] this example is an example which formed the source/drain in so perpendicular to the direction of crystal growth the direction in TFT shown in an example 10. That is, it is the example considered as the composition which a carrier moves as the direction which moves is perpendicular to the direction of a crystal growth and crosses the grain boundary of a needlelike or pillar-shaped crystal. If it is such composition, resistance between the source/drain can be made high. This is for a carrier to have to move so that the grain boundary of the crystal which carried out the crystal growth needlelike or pillar-shaped may be crossed. What is necessary is just to set up with what sense TFT is only prepared in the composition shown in an example 10, in order to realize composition of this example.

[0159] [Example 12] In the composition shown in an example 10, this example prepares TFT and is suitable (it defines by the line which connects the source / drain field here.). namely, -- the thing to which a carrier flows and for which it is suitable, and it comes out and the direction of TFT is opted -- carrying out -- let it be a summary to choose the property of TFT by setting up at the direction of a crystal growth to the substrate front face of a crystalline silicon film, and arbitrary angles

[0160] As mentioned above, since a carrier moves along with the grain boundary when moving a carrier in the direction of crystal growth, the mobility can be raised. On the other hand, since a carrier must cross many grain boundaries when moving a carrier in the perpendicular direction to the direction of crystal growth, the mobility of a carrier falls.

[0161] Then, the mobility of a carrier is controllable by setting up an angle between [of a crystal growth] these two states (i.e., the direction) and with the direction to which a carrier moves in the range of 0-90 degrees. Moreover, if another view is carried out, resistance between the source / drain field can be controlled by setting up the angle of the above-mentioned crystal-growth direction and the direction to which a carrier moves. Of course, this composition is applicable also to the composition shown in drawing 11 . In this case, the angle of the direction of crystal growth which rotates in the range whose nickel minute amount addition field 300 of the shape of a slit shown in drawing 11 is 0-90 degrees, and is shown by the arrow 305, and the line which connects the source / drain field will be chosen in the 0-90-degree range. And when this angle is close to 0 degree, mobility is large and can consider as composition with the small electric resistance between the source/drain. Moreover, when this angle is close to 90 degrees, mobility is small and resistance between the source/drain can consider as large composition.

[0162]

[Effect] It is prepared on a substrate and the non-single crystal silicon semiconductor film which has the crystallinity which moreover carried out the crystal growth in the direction parallel to a substrate front face is faced using for TFT. By doubling the flow direction of the carrier which moves in the inside of TFT with the direction where the crystal growth was performed, it can consider as the composition which moves along with the grain boundary of the crystal movement of a carrier grew up to be needlelike or pillar-shaped (in parallel), and ** which obtains TFT which has high mobility is made.

[0163] Moreover, since the metallic element for making the point which carried out the crystal growth promote crystallization concentrates and exists in the direction parallel to a substrate, the stability and reliability of operation of TFT can be raised by avoiding this field and forming TFT. Furthermore, introduce a catalyst element and it is made to crystallize at low temperature for a short time, and using the crystalline silicon film which irradiated a laser beam or strong light further, by producing a semiconductor device, productivity is high and can obtain a device with a sufficient property.

[Translation done.]

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3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

- [Drawing 1] The catalyst element concentration dependency of the stacking tendency in a crystalline silicon film is shown.
- [Drawing 2] It is a model view explaining a crystallization mechanism.
- [Drawing 3] The production process of an example is shown.
- [Drawing 4] The result of the X diffraction of a crystalline silicon film is shown.
- [Drawing 5] The production process of an example is shown.
- [Drawing 6] The result of the X diffraction of a crystalline silicon film is shown.
- [Drawing 7] The production process of an example is shown.
- [Drawing 8] The production process of an example is shown.
- [Drawing 9] The thickness of a crystalline silicon film and the relation of a stacking tendency are shown.
- [Drawing 10] The production process of an example is shown.
- [Drawing 11] The outline of an example is shown.
- [Drawing 12] The production process of an example is shown.
- [Drawing 13] It is the photograph in which the crystal structure of a silicon film is shown.
- [Drawing 14] It is the photograph in which the crystal structure of a silicon film is shown.
- [Drawing 15] It is the photograph in which the crystal structure of a silicon film is shown.
- [Drawing 16] It is the ** type view having shown the crystal orientation of a silicon film.
- [Drawing 17] The concentration of the nickel in a silicon film is shown.
- [Drawing 18] It is the photograph in which the state of a silicon thin film is shown.
- [Drawing 19] It is the ** type view having shown the crystallization mechanism of a silicon film.

[Description of Notations]

- 11 Glass substrate
- 12 Amorphous silicon film
- 20 Oxidization silicon film
- 14 Acetic-acid solution film containing nickel
- 15 ZUPINA
- 21 Oxidization silicon film for masks
- 22 Longitudinal-growth portion
- 23 A part for a horizontal growing region
- 13 Oxidization silicon film
- 104 ... Barrier layer
- 105 ... Oxidization silicon film
- 106 ... Gate electrode
- 109 ... Oxide layer
- 108 ... The source / drain field
- 109 ... A drain / source field
- 110 ... Layer insulation film (oxidization silicon film)
- 112 ... Electrode
- 113 ... Electrode
- 114 ... Channel formation field
- 201 ... Glass substrate
- 202 ... Ground film
- 203 ... Silicon film
- 205 ... Oxidization silicon film for masks
- 206 ... Puncturing portion
- 207 ... Acetic-acid solution film containing nickel
- 208 ... Barrier layer
- 209 ... Oxidization silicon film
- 210 ... Gate electrode

211 ... Oxide
212 ... Impurity range of N type
213 ... Impurity range of N type
214 ... Oxidization silicon film (layer insulation object)
215 ... Layer insulation object
217 ... An electrode and wiring
218 ... An electrode and wiring
301 Glass Substrate
302 Ground Film (Oxidization Silicon Film)
303 Mask
304 Silicon Film
305 The Direction of Crystallization
306 Gate Insulator Layer
307 Gate Electrode
308 Anodic Oxidation Layer
309 Gate Electrode
310 Anodic Oxidation Layer
311 Source / Drain Field
312 Channel Formation Field
313 Drain / Source Field
314 Source / Drain Field
315 Channel Formation Field
316 Drain / Source Field
317 Electrode
318 Layer Insulation Object
320 Electrode
319 Electrode
401 Glass Substrate
402 Ground Film (Oxidization Silicon Film)
403 Mask
404 Nickel Minute Amount Addition Field
405 Silicon Film
406 Gate Insulator Layer
407 Gate Electrode
408 Source / Drain Field
409 Channel Formation Field
410 Drain / Source Field
411 Layer Insulation Object
413 Electrode
414 Electrode
412 ITO (Pixel Electrode)
501 Crystal-Growth Side
502 Crystalline Silicon
503 Amorphous Silicon
504 The Apparent Direction of Crystal Growth
505 The Apparent Direction of Crystal Growth
506 Crystal-Growth Side

[Translation done.]

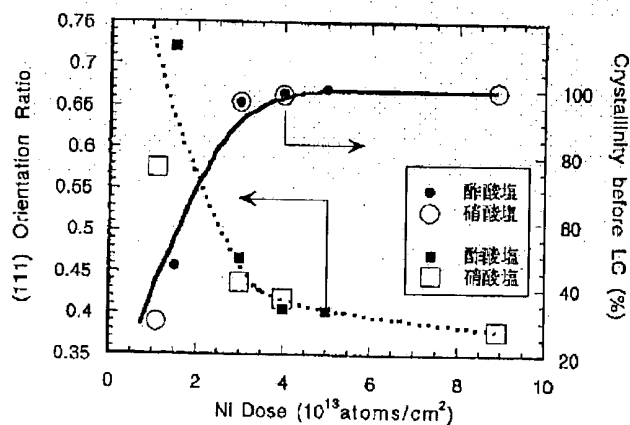
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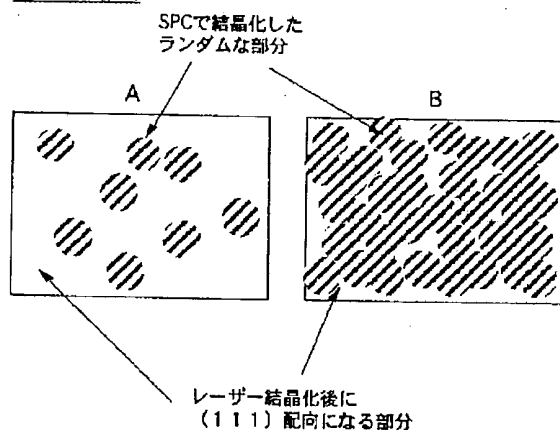
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DRAWINGS

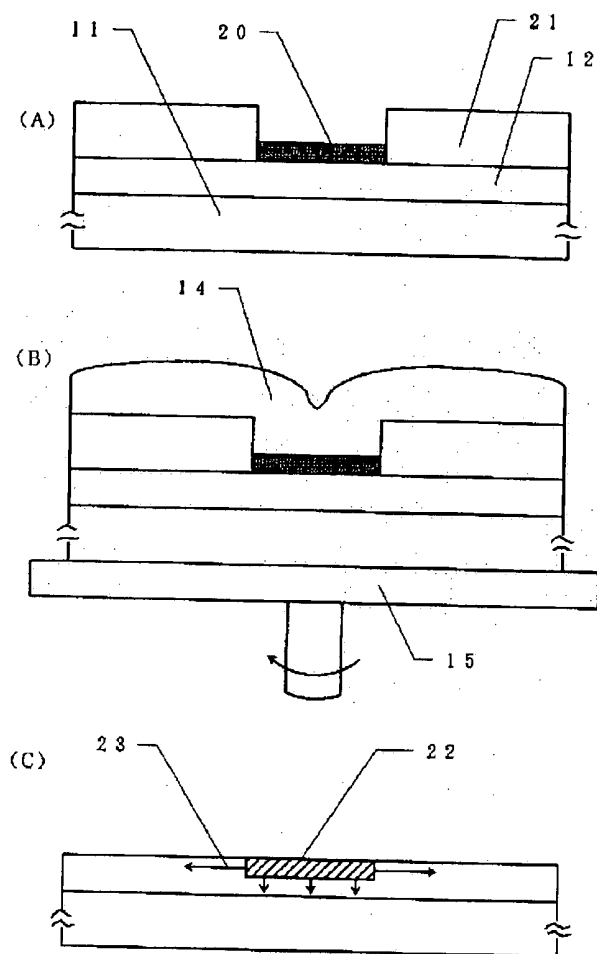
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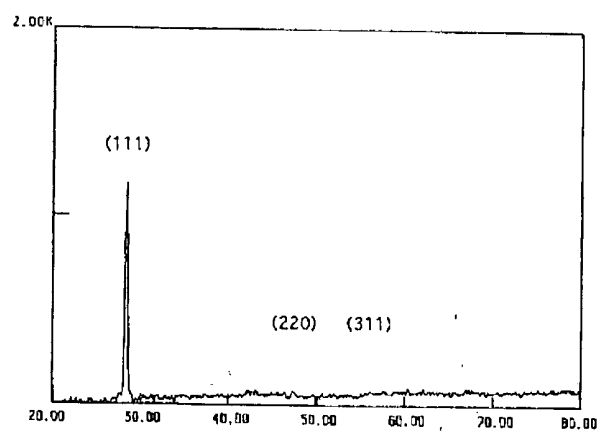
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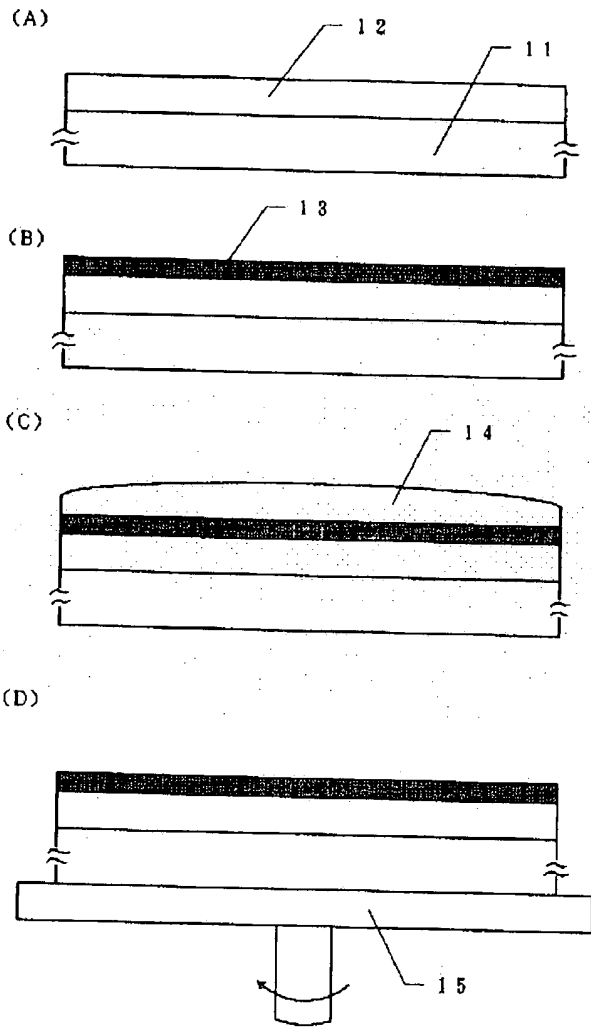
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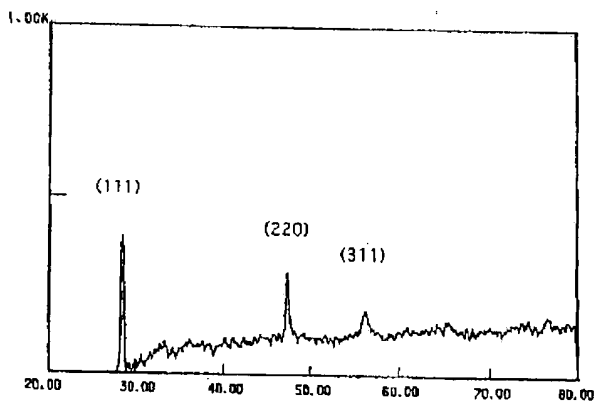
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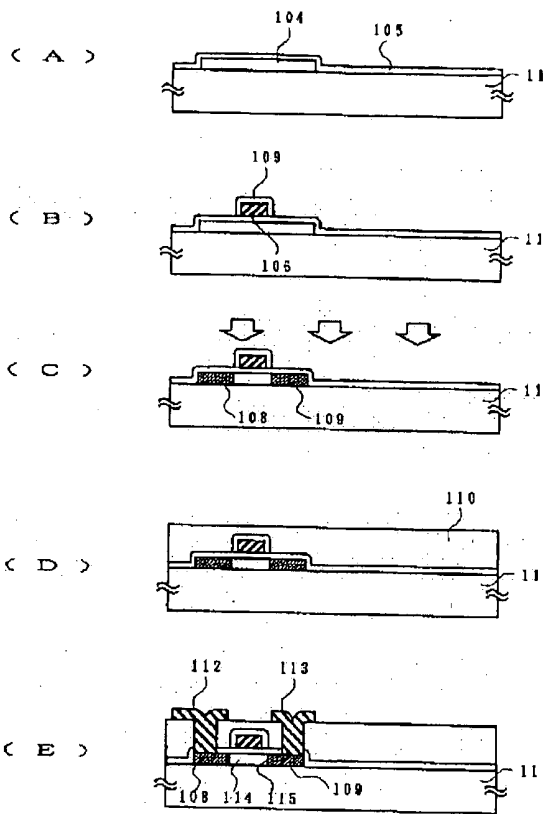
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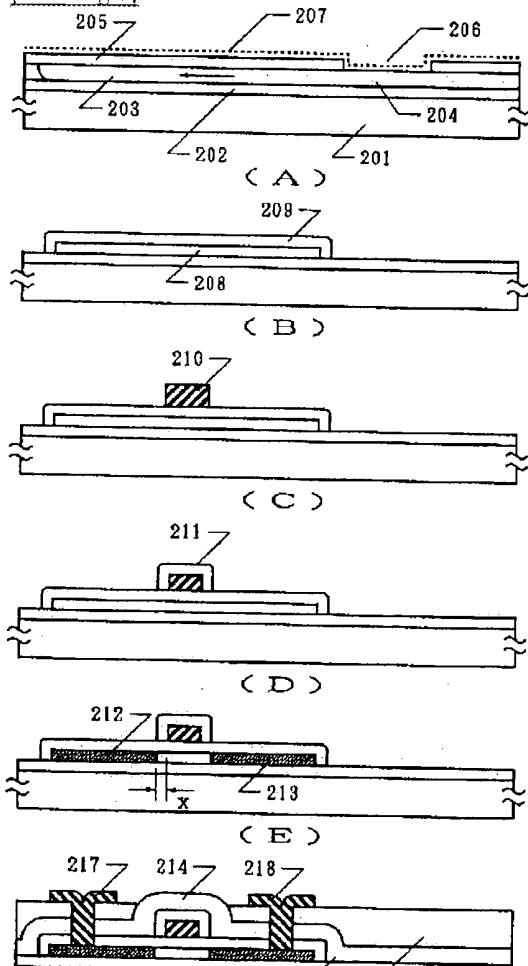
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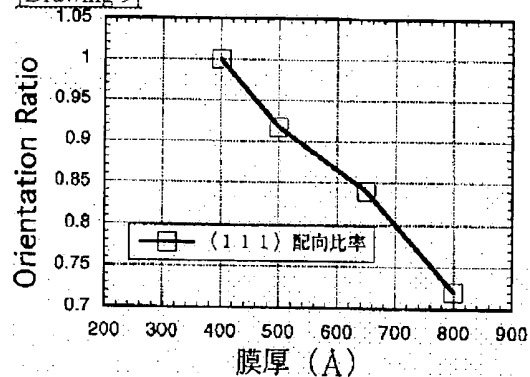
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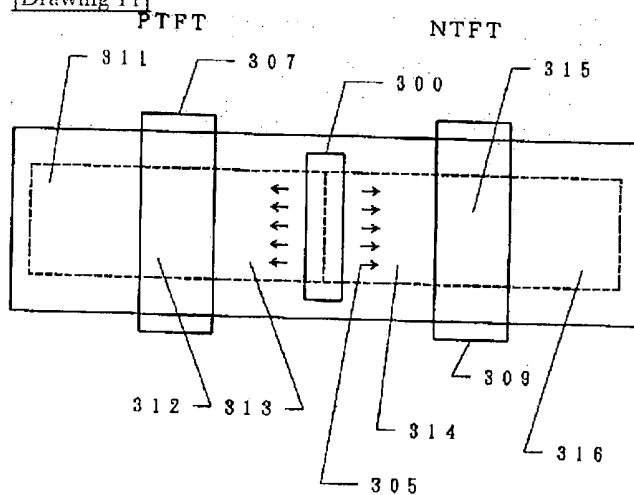
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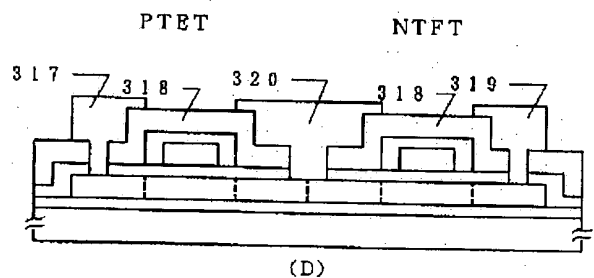
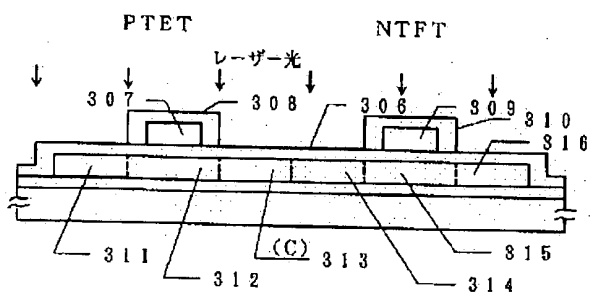
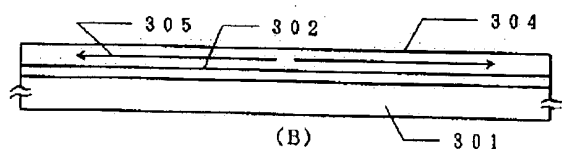
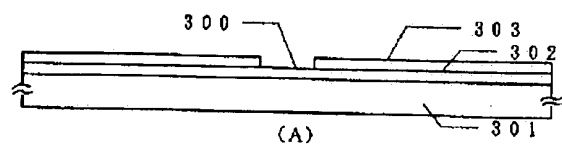
[Drawing 9]



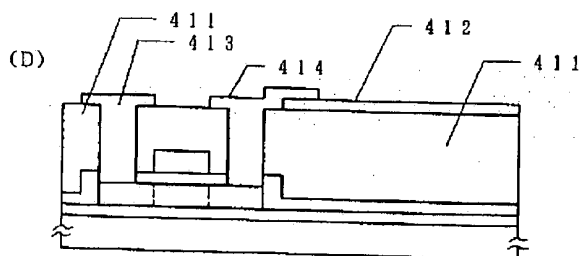
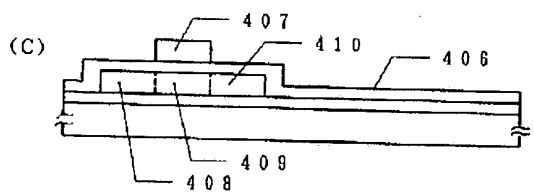
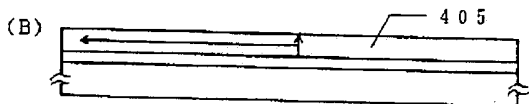
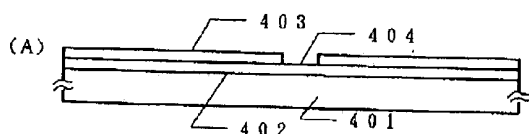
[Drawing 11]



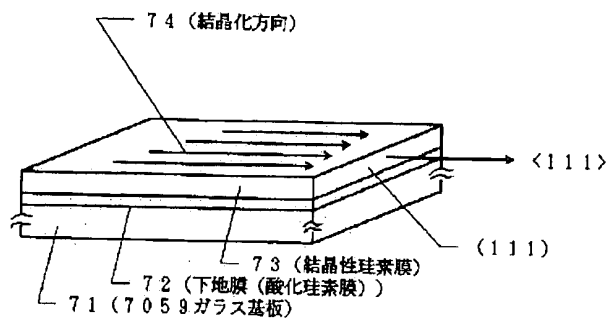
[Drawing 10]



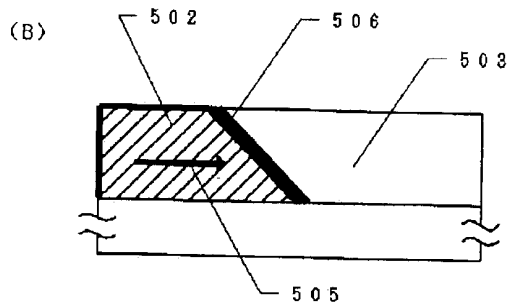
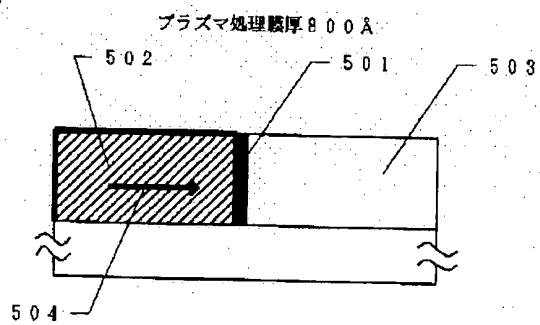
[Drawing 12]



[Drawing 16]



[Drawing 19]
 (A)

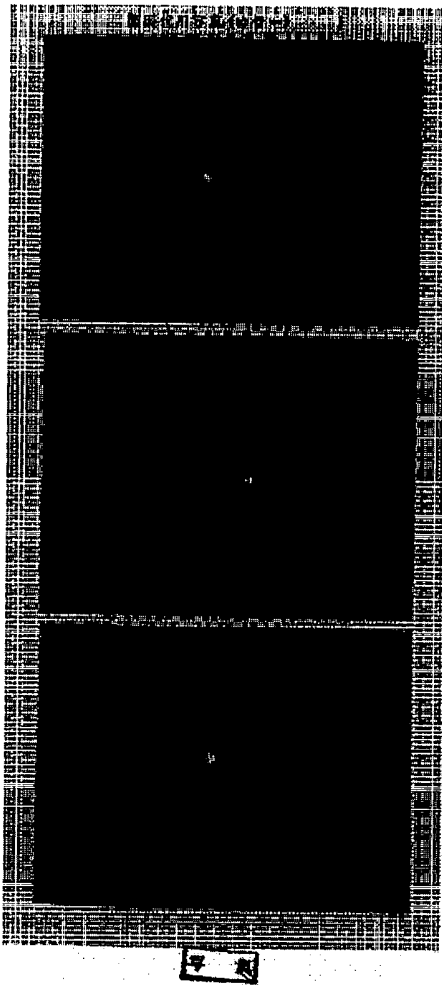


[Drawing 13]



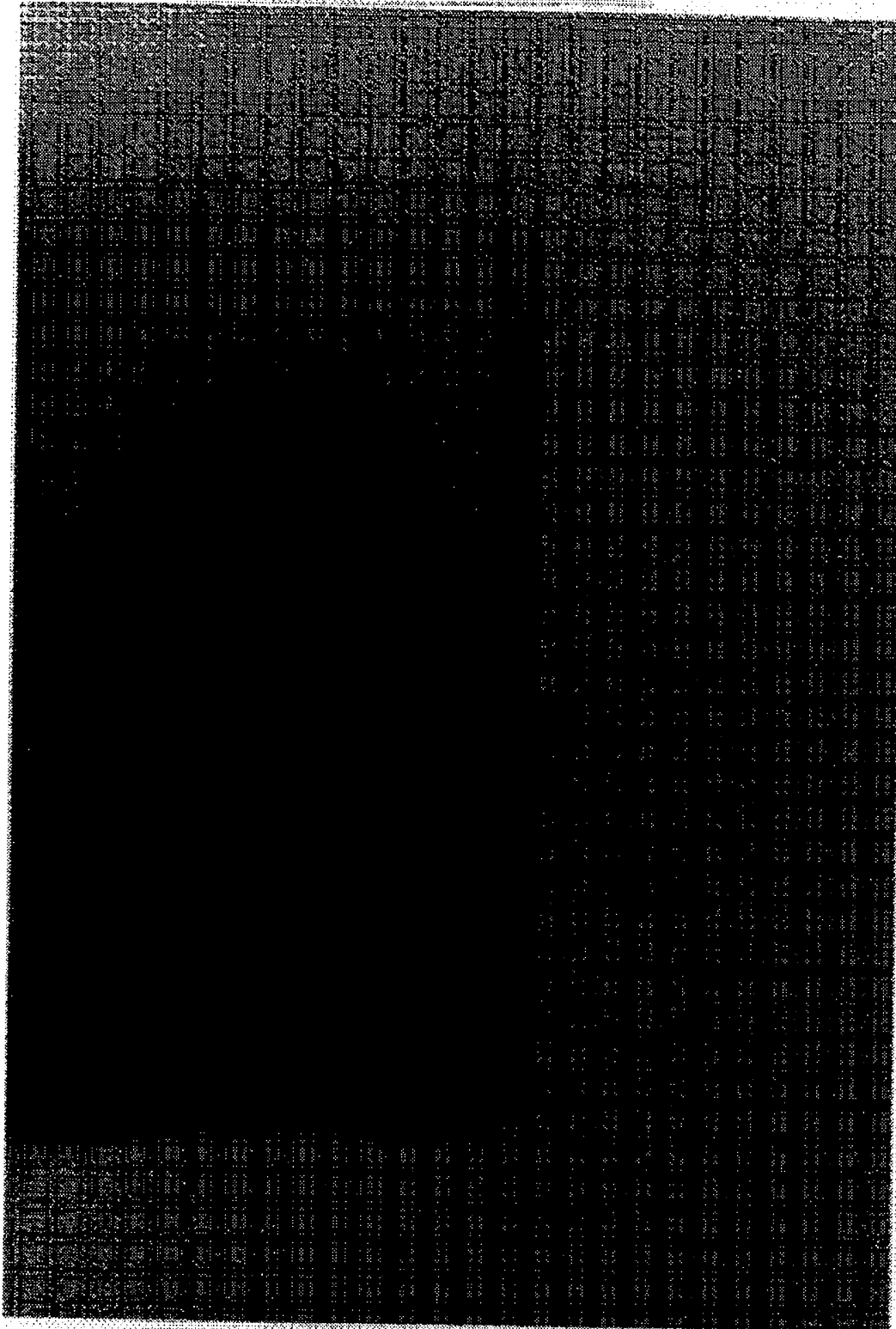
客 員

[Drawing 14]



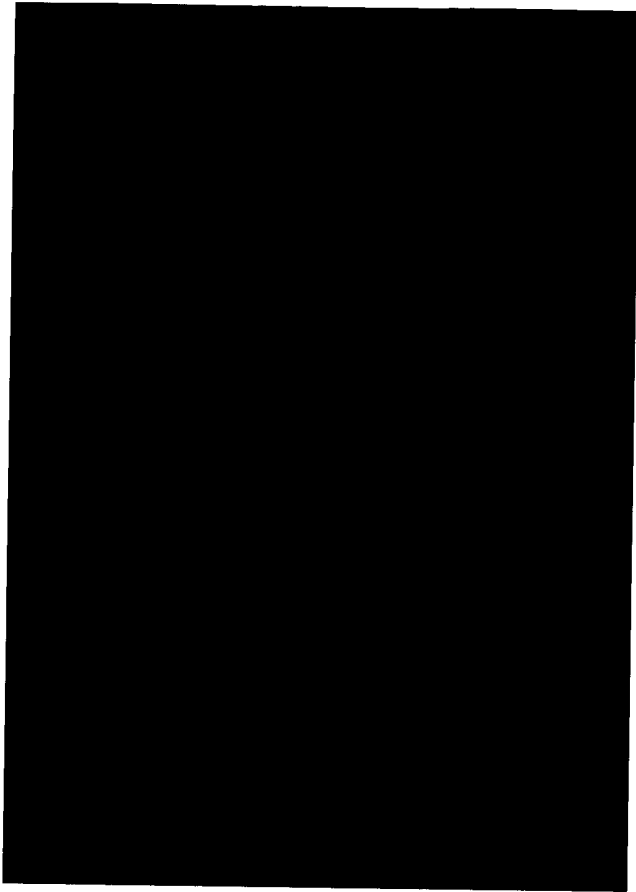
[Drawing 15]

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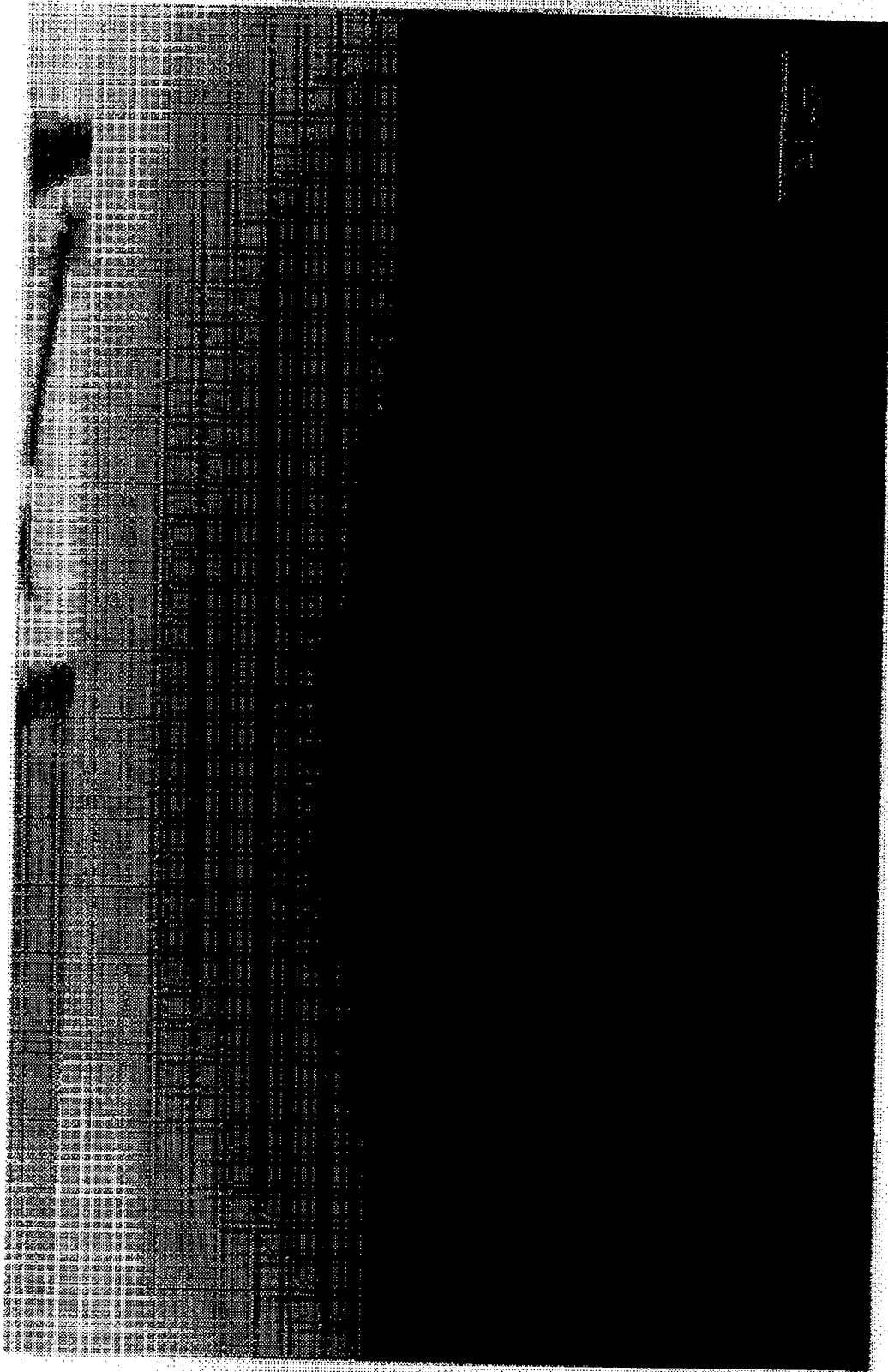
写真

[Drawing 17]



[Drawing 18]

図解乳品写真(カラー)



写真